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This final technical report describes the continual superconductivity research on the materials and structural phases responsible for the above 200-K superconducting transitions, their synthesis conditions, and the study of the physical properties associated with these transitions. Resistive transitions having superconducting-like character have been observed in multi-phase ceramic YBaCuO samples and on surfaces of nominal $YBa_2Cu_3O_7$ single crystals in the temperature range of 260 K to 340 K. The appearance of these transitions appears to require certain experimental measuring conditions including and oxygen atmosphere during measurements. Magnetization studies on these materials show a flux-trapping hysteretic behavior at similar temperatures, i.e., a more diamagnetic behavior in the zero-field-cooled-magnetization than the field-cooled-magnetization, which is characteristic of a weak superconducting phase being present. The synthesis conditions and structural information on multi-phase YBaCuO samples exhibiting reproducible flux-trapping phenomenon at 336 K is also detailed.

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1. *SUMMARY*

1.1 OBJECTIVES

The primary objectives of this superconducting research effort are:

(1) to understand the nature of the resistive and magnetic transitions observed near room-temperature,

(2) to identify the material conditions responsible for these transitions, and

(3) to improve the material characteristics as well as its properties.

The status on attaining these objectives is presented in the next section.

1.2 HIGHLIGHTS

Although this report describes in more detail our superconductivity research on materials responsible for the above 200-K superconducting transitions, their synthesis conditions, and their physical properties, we highlight some of the more important results in this section.

(i) experimental conditions for improving the probability of observing zero resistance transitions in YBaCuO samples near room-temperature

- measuring environment of 2 to 10 atms of O_2 gas pressure
- slow cooling to minimize flux trapping effects
- less than microampere measuring currents, preferably dc current

(ii) observation of resistance transitions above 200 K

- several ceramic samples of nominal 5:6:11 YBaCuO composition exhibited transitions in the 260 K to 300 K temperature range
- six nominal $YBa_2Cu_3O_{7-\delta}$ crystals exhibited transitions around 280 K and 340 K

(iii) magnetic characterization of flux-trapping hysteresis behavior near room-temperature

- zero-field-cooled magnetization (ZFCM) is more diamagnetic than the field-cooled-magnetization (FCM)
- the difference between the FCM and ZFCM decreases with increasing magnetic field strength with the ZFCM/H data approaching the FCM/H data

(iv) reproducible flux-trapping phenomena at 336 K in multiphase YBaCuO ceramic samples

- magnetic characterizations suggest transitions are superconducting in nature
- systematic DTA/TG studies indicate required synthesis conditions

1.3 PUBLICATIONS

L-Q. Wang, M.S.M. Minhaj, J.T. Chen, and L.E. Wenger, "Construction of a simple low-field solenoid for the Quantum Design@ SQUID magnetometer", Rev. Sci. Instrum. **64**, 3018 (1993).

M.S.M. Minhaj, S. Meepagala, J.T. Chen, and L.E. Wenger, "Thickness dependence on the superconducting properties of thin Nb films", *Phys. Rev. B* **49**, 15235 (1994).

M.S.M. Minhaj, J. Obien, D-C. Ling, J.T. Chen, and L.E. Wenger, "Magnetization studies of near-room-temperature phenomenon in CuO-based materials", *J. of Supercond.* **7**, 715 (1994).

M.S.M. Minhaj, David J. Thompson, L.E. Wenger, and J.T. Chen, "Paramagnetic Meissner Effect in a niobium disk", *Physica C* **235-240**, 2519 (1994).

D-C. Ling, K. Chang, J.T. Chen, and L.E. Wenger, "Observation of microwave induced dc voltages in a $YBa_2Cu_3O_{7-\delta}$ single crystal", *Physica C* **235-240**, 3291 (1994).

1.4 PRESENTATIONS

Papers presented:

American Physical Society meeting, 21-25 March 1994, Pittsburgh, PA.

- "Observation of a 336-K transition in mixed-phase YBaCuO samples", J. Obien, M.S.M. Minhaj, David J. Thompson, L.E. Wenger, and J.T. Chen.
- "Microwave effects in $YBa_2Cu_3O_{7-\delta}$ single crystals", D-C. Ling, K. Chang, J.T. Chen, and L.E. Wenger.

Spring Meeting of the Ohio Section of the APS, 13-14 May 1994, Cleveland, OH.

- "Paramagnetic Meissner Effect in a niobium disk", M.S.M. Minhaj, David J. Thompson, L.E. Wenger, and J.T. Chen.
- "Observation of magnetic-field interference patterns in a $YBa_2Cu_3O_{7-d}$ single crystal", D-C. Ling, Grace Yong, J.T. Chen, and L.E. Wenger.

International Conference of Materials & Mechanisms of Superconductivity - High Temperature Superconductivity - IV, Grenoble, France, 5-9 July 1994.

- "Paramagnetic Meissner Effect in a niobium disk", M.S.M. Minhaj, David J. Thompson, L.E. Wenger, and J.T. Chen.
- "Observation of microwave induced dc voltages in a $YBa_2Cu_3O_{7-\delta}$ single crystal", D-C. Ling, K. Chang, J.T. Chen, and L.E. Wenger.

Seminars presented:

L.E. Wenger

- "Search for Room-Temperature Superconductivity" University of Michigan, Ann Arbor, MI, 1 February 1994.
- "Evidence for Room-Temperature Superconductivity" University of Utah, Salt Lake City, UT, 17 February 1994.
- "High-Temperature Superconductivity Research" Wright Laboratories, WPAFB, Dayton, OH, 16 March 1994.
- "The Quest for Room Temperature Superconductors", Purdue University, West Lafayette, IN, 30 September 1994

J.T. Chen

- "Present Status of Superconducting-like Anomalies in Cuprates above 200 K", Texas Center for Superconductivity, University of Houston, TX, 4 November 1994.

1.5 PERSONNEL

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	J. Obien (AFOSR-91-0319)
	David J. Thompson (AFOSR-93-1-0321)
	Grace Yong (AFOSR-93-1-0321)
Degrees Awarded:	M.S.M. Minhaj, Ph.D.
	Thesis Title: "Fabrication and Magnetic Characterization of Layered Superconductors"
	14 October 1994
	D-C. Ling, Ph.D.
	Thesis Title: "An Investigation of Electrodynamic Properties of High-T_c Superconducting $YBa_2Cu_3O_{7-\delta}$ Single Crystals"
	15 December 1994

2. *INTRODUCTION*

With the reports of certain lanthanum copper oxides being superconducting above 30 K by Bednorz and Müller in 1986,[1] a revival of superconductivity research was forthcoming with discovering higher T_c materials being a real possibility. By February 1987, Wu *et al.* [2] reported that a multi-phase YBaCuO compound exhibited superconducting properties above liquid nitrogen's boiling point of 77 K. Other researchers were soon able to reproduce these experimental results and determine the superconducting phase to be $YBa_2Cu_3O_{7-\delta}$ ($\delta<0.5$) with a T_c of 93 K.[3,4] The onslaught of research that followed was permitted in part by the ease of synthesizing the ceramic samples of these oxides under normal atmospheric conditions by a solid state reaction technique. Within the year both $Bi_2Sr_2Ca_{1+n}Cu_{2+n}O_{8+2n}$ and $Tl_2Ba_2Ca_{1+n}Cu_{2+n}O_{8+2n}$ (n=0,1,2) were found to exhibit superconducting properties with $Tl_2Ba_2Ca_2Cu_3O_{12}$ having a T_c of 128 K.[5] This material remained as the highest T_c superconductor until the summer of 1993 when HgBaCaCuO compounds having a 135-K critical temperature were discovered.[6,7] One of the reasons for the lengthy time interval before the HgBaCaCuO compound was discovered was the increased complexity required in the synthesis of the material. In order to attain the correct perovskite structure, HgBaCaCuO compounds must be synthesized under 5 GPa of pressure at 950°C followed by an oxygen anneal. In addition to these superconductors, there are currently several other different families of oxide superconductors having the defect perovskite structure.

These aforementioned materials have satisfied the following criteria for being classified as superconducting materials:

(i) the disappearance of resistance at T_c

(ii) the appearance of a Meissner (diamagnetic) response at T_c

(iii) a well-established characterization of the crystalline structure associated with the superconducting phase

(iv) reproducible properties and synthesis conditions performed at other laboratories.

Thus materials having satisfied these criteria are widely accepted as being bulk superconductors. Nevertheless, there have been numerous reports and publications of sharp resistive transitions[8-15] and other superconducting-like phenomena[16-19] at much higher temperatures, even approaching room temperature. Unfortunately these higher-temperature phenomena were one- or two-time occurrences as they had an inability to

survive repeated thermal cyclings through their transition temperatures. In 1989, we observed zero-resistance states with transition temperatures above 200 K in multi-phase YBaCuO materials maintained in an oxygen atmosphere.[13,14] Using a multiple-lead arrangement, resistance and current-voltage (I-V) measurements were performed on multi-phase $Y_5Ba_6Cu_{11}O_X$ ceramic samples. The results for several samples showed zero-resistance T_C's in the temperature range of 235 K to 250 K for various electrical paths that withstood repeated thermal cycles. In addition, the resistance of the sample was found to decrease with each of the first three thermal cycles. Furthermore, the resistive drops along preferential directions indicated that several possible superconducting phases might be present in this sample. Thus these results strongly suggested the existence of higher-T_C phases in these materials and not simply some experimental artifact. However, the nature of these transitions was still somewhat uncertain since subsequent investigations on these oxide materials had not always shown similar resistive transitions nor exhibited bulk-like characteristic properties associated with superconducting transitions, e.g., a diamagnetic response in the magnetization. Thus the present AFOSR program entitled "Investigations of YBaCuO Superconducting Materials with T_C above 200 K" focuses on a study of these near-room-temperature phenomena in order:

(1) to understand the nature of the resistive and magnetic transitions observed near room-temperature,

(2) to identify the material conditions responsible for these transitions, and

(3) to improve the material characteristics as well as its properties.

In the next sections, we review the status of this research over the past 18 months as well as our present understanding of the remaining problems.

3. *STUDIES ON CERAMIC MULTI-PHASE YBaCuO SAMPLES*

In our studies, one critical condition for observing and reproducing a zero-resistance transition having a T_c above 200 K is to keep the specimen in an O_2 environment continuously during the electrical measurements as it is thermally cycled through the transition temperature. However in other experiments, such as microwave and magnetization measurements, anomalous high-T_c phenomena can be observed even when the specimens are not kept in an oxygen environment. One possible explanation for these different experimental observation conditions is that diffusion of oxygen molecules into a solid at room temperature is limited. Thus this process results in only the material near the surfaces of grains being affected by the oxygen diffusion and the formation of the higher-T_c material. In the microwave and magnetization measurements, disconnected granular shells can still contribute to an observable signal even though flux trapping can dominate the magnetization response. However, the observation of zero-resistance requires a continuous path of these "good" surfaces, i.e., good connectivity between the granular shells of the higher-T_c material. In order to determine the effect of low-temperature oxygen diffusion on the granular YBaCuO materials, the resistance of several multi-phase $Y_5Ba_6Cu_{11}O_y$ ceramic samples were monitored over time while continuously being maintained in an O_2 gas at 2 to 10 atms of pressure and temperatures up to 380 K. Typically, the resistance of the samples decreased at room temperature with decreases as large as an order of magnitude. Also the temperature dependence below 300 K changes from linear to a concave upwards behavior, a clear indication of a material change caused by the low-temperature oxidation. (See Fig. 3-1.) This oxidation results from an increase in the volume fraction of the higher-T_c superconducting phase and an increase in the conductivity of the intergranular regions, both contributing to overall resistance decrease. However repeated thermal cyclings can also have a deleterious effect on the intergranular coupling as the thermal expansion and contraction between grains can result in poorer mechanical contact. We believe this later effect can dominate the measured resistance in the ceramic YBaCuO samples and prevents electrical measurements from showing zero-resistance transitions more frequently in these samples.

Even though there is difficulty in observing zero-resistance transitions in these multi-phase ceramic samples, indications of superconductivity by the appearance of a hysteretic behavior between the zero-field-cooled-magnetization (ZFCM) and the field-cooled-magnetization (FCM) are observed more frequently. However these magnetic results are

less conclusive for a superconducting transition since a truly diamagnetic response below these higher transition temperatures has not been observed to date. During this same period, one-third (5 out of 15) of the nominal $Y_5Ba_6Cu_{11}O_y$ ceramic samples measured in our SQUID magnetometer exhibited a hysteretic behavior near room temperatures. This hysteretic behavior is typified by a weak, temperature-dependent divergence of the ZFCM from the more paramagnetic-like FCM. (See Fig. 3-2.) The FCM above 100 K can be totally accounted for by adding the magnetic contributions from the major crystalline phases found in these 5:6:11 samples ($YBa_2Cu_3O_7$, Y_2BaCuO_5, and CuO) and from the sample holder. Thus any differences in the ZFCM from the FCM can be attributed to other minority phases in the sample, including higher-T_c superconducting phases. For such a superconducting phase in a predominately paramagnetic host material, one would expected that the ZFCM to be less paramagnetic than the FCM since a small diamagnetic response would be generated by the induced shielding currents (flux exclusion) when the magnetic field is applied after cooling below T_c in zero field. For larger magnetic fields, one would expect the zero-field-cooled susceptibility ZFCM/H to be less diamagnetic and approach the FCM/H data as shown in Fig. 3-3. Likewise no detection of the superconducting transition in the FCM measurements would be expected since flux trapping in these thin and probably discontinuous superconducting granular surfaces would cancel the diamagnetic shielding contribution.

One of these ceramic $Y_5Ba_6Cu_{11}O_y$ samples after a lengthy high-pressure oxygen anneal (over 10 atm O_2 for nearly one month at 100°C) exhibited a more distinctive, superconducting-like transition at 310 K for two different magnetic fields as shown in Fig. 3-4. The ZFCM deviates from the paramagnetic-like FCM over a 10-K temperature range and maintains a nearly constant diamagnetic difference from the FCM at lower temperatures, as if the ZFCM response simply consists of a diamagnetic response from a small "bulk-like" superconductor and a paramagnetic response from a much larger non-superconducting material. In addition, there are discontinuities (jumps) in the ZFCM data in the temperature range between 270 K and 290 K. These discontinuities always tend to go from a more diamagnetic response at lower temperatures to a more positive response at higher temperatures, very reminiscent to flux jumps observed in some inhomogeneous superconducting materials.

In summary, the aforementioned electrical and magnetic features near room temperature are consistent with superconducting transitions in multi-phase samples where the

nonsuperconducting regions dominate the overall measured responses. These properties are consistent with thin material phases that reside on or near the surfaces of the 1-2-3 granules. In fact, these phases may be the result of an interfacial region having a thickness of 10 to 100Å. This thickness would result in very small critical currents and thus explain the difficulty in observing zero-resistance transition. Similarly, this thickness would be substantially less than the penetration depth and correspondingly suppress the diamagnetic response in the magnetization measurements. Until this higher-T_c superconducting phase can be synthesized in a greater volume fraction in these ceramic samples, the reproducibility of zero-resistance transitions and clear diamagnetic transitions will be quite small. A more successful approach is suggested in the next section describing our work on nominal $YBa_2Cu_3O_{7-\delta}$ single crystal samples.

4. *STUDIES ON NOMINAL $YBa_2Cu_3O_{7-\delta}$ SINGLE CRYSTAL SAMPLES*

As we first reported in 1991, we have observed a strong anisotropic behavior in the electrical resistance on several nominal $YBa_2Cu_3O_{7-\delta}$ single crystal samples grown in our laboratory.[15] This anisotropic behavior is characterized by the resistance along the *c* -axis exhibiting a semiconducting-like temperature dependence until 90 K where the well-known superconducting transition of the 1-2-3 superconducting phase occurs, while zero-resistance transitions are observed in the 240 K to 270 K range for currents along the surfaces (*a-b* plane) of these crystalline samples. Since the oxidation studies on the ceramic YBaCuO samples indicate surface oxidation may lead to the observation of near-room-temperature resistive transitions, we have returned to performing more electrical and magnetic measurements on nominal single crystals during this contract period.

Extensive electrical measurements on over a dozen crystal samples in oxygen pressures as high as 10 atms indicate the importance of maintaining an O_2 environment around the sample during the measurements, especially if reproducible resistive transition are to be observed near room temperature. Secondly, extreme care must be taken while cooling the sample through the transition region as flux trapping can occur which can lower the T_c, diminish the size of the resistive change, or even eliminate the observation of the resistive transition as the higher resistance state is maintained. The flux trapping cannot only occur because of the presence of stray magnetic fields but also by self-fields generated by external bias currents or thermal emfs. Consequently, slow cooling of the sample through the transition in the absence of any current is the preferred technique for performing electrical measurements.

Of these samples (from three batches of crystals), six measured in 1 atm of O_2 exhibited small bumps or changes in slope in the vicinity of 280 K which indicate some electrical property change; however, the data is inconclusive as to whether these features can be associated with a superconducting transition or not. Three other samples measured in 10 atm of O_2 clearly show resistive changes in the vicinity of 340 K and 280 K. The resistive data for one particular sample (#GY0026D-2) can be fairly well understood in terms of two superconducting transition temperatures. The 340-K transition was observable in the plane of the crystalline platelet sample and only during the warming cycle after cooling in zero current. (See Fig. 4-1.) A high resistive state of approximately 2 Ω can easily dominate the lower-temperature measured resistive features if a bias current was applied before cooling through the transition. The resistive transition at 280 K showed a hysteretic

behavior with a lower T_c measured during the cooling cycle and a larger T_c during the warming cycle as seen in Fig. 4-2. These features are very analogous to the hysteretic behavior observed in a weak-link superconductor or a conventional Josephson junction with a very small critical current. The presence of a bias current in these weak superconducting junctions creates a large enough self-field to lower the transition temperature or even completely suppress the transition. Consequently we speculate that both of these transitions are superconducting in nature even though the resistance never goes to zero. This interpretation is further supported by the magnetization studies which show a hysteretic behavior between the zero-field-cooling and field-cooling measurements developing at similar temperatures.

Of 13 nominal single crystal samples measured in the SQUID magnetometer, four exhibited near-room-temperature hysteretic behavior, i.e., the zero-field-cooled-magnetization (ZFCM) became increasingly more diamagnetic than the field-cooled-magnetization (FCM) below the transition temperature as clearly shown in Fig. 4-3 for an applied field of 100 Oe. However, it should be pointed out that the magnetization for most of those samples not exhibiting a hysteretic behavior were performed in fields of less than 5 Oe which might have resulted in not enough sensitivity for detecting a difference between the ZFCM and the FCM responses at these low field strengths. For two samples including one from a single crystal batch exhibiting near-room-temperature resistive transitions, the magnetic hysteresis develops at about 310 K with an uncertainty of $\pm$ 10 K due to instrumental scatter of the data. For fields between 50 and 250 Oe, the FCM/H data (FCM divided by the applied magnetic field H) are essentially the same; however, the ZFCM/H data are independent of field for lower field strengths and for the larger fields increase towards the FCM/H data resulting in a smaller hysteresis as shown in Fig. 4-4. Thus the ZFCM/H becomes less diamagnetic with respect to the FCM/H for increasing field strengths even though the overall magnetic response is positive in sign. This behavior is qualitatively similar to the magnetic susceptibility for an inhomogeneous superconductor where ZFCM/H has its maximum diamagnetic response for the lowest field strengths and decreases towards zero for larger fields when the field is greater than the lower critical field H_{c1}. The FCM/H is always less diamagnetic than the corresponding ZFCM/H and can even be zero for low fields if the flux trapping is nearly equal to the diamagnetic flux exclusion response due to the increasing viscous nature of flux with decreasing temperature. For granular superconducting samples, the FCM/H is typically one-third of

the maximum ZFCM/H result; however, this fraction can be substantially reduced if the superconducting sample has large interior regions of non-superconducting areas and strong pinning sites as is the probable case for the nominal single crystal samples.

Figures 4-5 to 4-7 show the magnetic behavior of a third sample (#GY0026D-2) which is the same one exhibiting the resistive drops at 280 K and 340 K shown in Figs. 4-1 and 4-2. The ZFCM/H and FCM/H results are qualitatively similar to those described in the preceding paragraph, except the hysteresis begins in the vicinity of 340 K and the ZFCM/H and FCM/H at 500 Oe nearly coincide. Although the sign of the magnetic responses are positive, the relative magnetization changes between the ZFCM/H and the FCM/H show a diamagnetic-like character. This diamagnetic character can be further enhanced by noting that the FCM/H data for 500 Oe can be fit to the normal-state susceptibility measured for a single-phase 1-2-3 sample as indicated by the solid lines in these figures. Thus not only does the ZFCM/H data indicate the presence of a diamagnetic response below 340 K, but the FCM/H data for the lower fields is also diamagnetic in nature and becomes more diamagnetic for lower field strengths as well. The magnetization results for another nominal single crystal sample (#GY0026D-1) from the same batch exhibit nearly identical behavior for similar field strengths. The overall similarity of this magnetic behavior to that for an inhomogeneous superconductors supports the conclusion that these crystalline samples have a superconducting phase with a T_c near 340 K, in agreement with the electrical measurements. The microstructure of this sample is presently being investigated by transmission electron microscopy (TEM) studies by C.H. Chen at AT&T in order to determine if defect structures similar to previous TEM results on our samples are present. Because of the increased experimental success in the detection of superconducting-like phenomena in the nominal $YBa_2Cu_3O_{7-\delta}$ single crystal samples, we plan to continue electric and magnetic measurements on these type of samples.

5. *STUDIES ON MATERIALS EXHIBITING A 336-K TRANSITION*

As reported in an earlier Technical Report (AFOSR-91-0319 Annual Report for 1992-93), unusual magnetic transitions have been observed at 336 K for three different batches of granular YBaCuO samples. These transitions are characterized by the zero-field-cooled-magnetization (ZFCM) being featureless with only a weak temperature dependence in the range of 300 K to 360 K while the field-cooled-magnetization (FCM) shows a fairly sharp, positive increase below 336 K which remains essentially a constant value above the ZFCM at lower temperatures as shown in Fig. 5-1. Although this magnetic behavior is uncharacteristic for a bulk superconductor at its transition temperature, we have observed resistive drops in the same temperature range in other ceramic YBaCuO samples and nominal $YBa_2Cu_3O_{7-d}$ single samples. (See preceding two sections.) Furthermore, one of the earliest reports of zero-resistance transitions above room temperature was at 340 K in a $YBaSrCu_3O_7$ sample reported by a Japanese group.[10] The strong coincidence in the 340-K temperature between these various superconducting-like results suggests a more thorough study should be pursued. We have correspondingly pursued a three prong attack to this problem. (i) We have systematically studied the synthesis conditions for growing samples which exhibit this 336-K transition by utilizing our simultaneous differential thermal analyzer and thermogravimetry (DTA/TG) system. (ii) Subsequently we have utilized x-ray diffraction (XRD) and electron microscopy to assist in the identification of possible crystal phases and/or structural feature that could be associated with the appearance of the 336-K transition. (iii) In addition, we have tried to characterize the nature of this transition more fully and its possible relation to surface superconductivity. During the past 18 months, over ninety ceramic YBaCuO samples were tested for the possible existence of the 336-K transition by low-field magnetization measurements, with nearly 40% exhibiting some indication of this unusual magnetic behavior.

The first phase of this research was to repeat the synthesis conditions utilized in the previous preparation of nominal $Y_5Ba_6Cu_{11}O_y$ samples exhibiting this 336-K magnetic transition. Five different batches of 5:6:11 (Y:Ba:Cu) nitrate and oxide powders were mixed and homogenized in a nitric acid solution. After heating to 950°C in flowing O_2 for 18 hours, the reacted powders were quenched to room temperature in air. This procedure was repeated four more times with intermediate grindings. Out of the five batches, samples from only two batches clearly exhibited the characteristic magnetic behavior at 336 K. (See Fig. 5-1 for the magnetic characteristics for a sample from these batches.) Even though the

synthesis conditions were the same, the lack of total reproducible results indicated a more systematic and informative approach to the synthesis procedure, such as afforded by the DTA/TG system, would be beneficial. This is especially true since a knowledge of the reaction processes during the cooling cycle could be easily monitored.

Utilization of the DTA/TG system in the sample synthesis permitted the variation of several parameters including the relative O_2 partial pressure, the inert gas to be utilized, different final heating temperatures, different hold times at the highest temperatures. Also variations in the relative Y:Ba:Cu compositions as well as in starting materials were tested. (See Table I.) The following summarizes our findings of the synthesis conditions for increased probability of growing samples which will exhibit the 336-K magnetic transition.

(1) Heating the powders /samples to temperatures above their peritectic transformation temperature.
(2) Reducing the O_2 partial pressure.
(3) Heating in a pure Ar gas flow rather than in He or N_2 gas flow.
(4) Presence of a sharp solidification peak in the DTA data during the cooling cycle. (See Fig. 5-2.)
(5) Appearance of an exothermic peak during the cooling cycle (852°C in flowing Ar) with a barely detectable weight gain. This weight gain is presumably an oxygen uptake from the surrounding gaseous environment which still contains some oxygen present from the sample's oxygen loss during the heating cycle. (See Fig. 5-2 to 5-4.)
(6) Appearance of 336-K magnetic transition only dependent upon initial synthesis cycle of sample. The magnitude of the difference between the FCM and the ZFCM was found to be unchanged by subsequent thermal treatments in Ar or anneals in O_2.
(7) Starting compositions or materials play a secondary role in the formation of samples exhibiting the 336-K transition.

It must be pointed out that the interplay between the exothermic peaks listed in (4) and (5) and their correlation to the appearance of the 336-K transition is still unclear at the present time and further studies are continuing. Also since the majority of these samples were grown in flowing Ar and not pressed into pellets, the samples are highly resistive, or even insulating, and thus electrical measurements are not available.

Table I. DTA/TG Synthesized Samples with 336-K Transition

Nominal Composition (Y:Ba:Cu)	Starting Materials	Nitric Acid Solution
1 : 2 : 2.75	nitrates & oxides powders	yes
1 : 2 : 4	$YBa_2Cu_4O_8$	no
4 : 5 : 9	$YBa_2Cu_4O_8$ & Y_2BaCuO_5	no
4 : 5 : 9	carbonates	no
4 : 5 : 9	nitrates & oxide powders	yes

Structural and surface studies by XRD and SEM are not complete at this time. Initial XRD data indicate a few common features present in those samples exhibiting the 336-K transition. First, the predominate phases are the tetragonal $YBa_2Cu_3O_{6.5}$ and the insulating Y_2BaCuO_5 structures with smaller amounts of CuO and $BaCuO_2$. However two sets of peaks associated with the tetragonal 1-2-3 phase are anomalous: the intensities of the (103)/(013) and (110) peaks are nearly equal in magnitude although the ratio should be closer to 2:1; and the relative intensities for the (003) and (100)/(010) do not agree the literature values. (See Fig. 5-5 to 5-7.) This suggests a possible distortion of the lattice or chemical substitution for certain atoms in these particular planes. Furthermore because the maximum temperatures during the DTA/TG synthesis of these samples exceed the peritectic temperature, these samples have substantial melting occurring which is supported by the SEM topographical studies. Moreover, the SEM photos (see Fig. 5-8) indicate significant melting had occurred even on the quenched 5:6:11 sintered samples that had only been heated to 950°C in O_2, nearly 20°C below its corresponding peritectic temperature.

The last aspect of this research is the study of the nature of this 336-K transition. Initially a comprehensive investigation of the magnetic field dependence of both the ZFCM and FCM were undertaken. The abrupt, positive increase in the FCM below 336 K was found to be present at all fields from 0.5 Oe to 200 Oe, although the increase was essentially field independent. The ZFCM began to exhibit a similar increase just below 336 K for fields above 10 Oe as shown in Figs. 5-9 to 5-11. This behavior is reproducible as

measurements repeated many times on a given sample resulted in the same ZFCM and FCM within the sensitivity of the SQUID magnetometer. Some of the measurement were performed after the sample had been placed in a desiccator for two years. In addition, the change in the sample orientation and after pulverization of a sample had no effect on the observed magnetic behavior nor the 336-K transition temperature.

These features associated with the 336-K transition can be understood in terms of two possible effects: the presence of a small amount of ferromagnetic impurities or a strong flux pinning around paramagnetic inclusions. Even though the starting materials of the oxides, carbonates, and nitrates used in the preparation of the YBaCuO samples are of high purity (>99.9 % purity), there is always a trace amount (few parts per million) of metal impurities present in these materials with the most common ferromagnetic impurity being iron or iron oxide. Other possible ferrimagnetic materials in the YBaCuO samples could be yttrium iron garnet and barium ferrite which have Curie temperatures in the 500 to 800°C range. Clearly, the 336-K transition occurs well below their respective Curie temperatures and thus cannot be attributed to these impurities. Furthermore, if ferromagnetic or ferrimagnetic impurities were present in the starting materials then it should be present in all the samples prepared from the same starting materials and one should therefore expect all samples to exhibit the features associated with the 336-K transition. In contrast, less than half exhibit the observed features. Also, the magnetization difference (FCM-ZFCM) as a function of magnetic field saturates in a few oersteds. (See Fig. 5-12.) This value is extremely small for magnetic transitions such as for a ferromagnetic material. Thus we can exclude the possibility of the 336-K transition being due to the presence of these ferromagnetic or ferrimagnetic impurities.

The other possibility would be the existence of a thin layer of a 336-K superconducting material surrounding a paramagnetic inclusion. It is observed that the ZFCM data is essentially featureless in the transition region of 336 K at the lowest fields. If the penetration depth of this superconducting phase is comparable to the dimensions of the superconducting layers, the diamagnetic response (or flux exclusion) would be substantially suppressed so that the ZFCM might be nearly zero. In addition, this signal would be superimposed upon a more dominant paramagnetic background that arises from the nonsuperconducting regions (123, 211, and CuO) of the sample above 100 K. Whereas for the FCM, these 336-K superconducting layers would trap magnetic vortices (flux) with the field inside the vortex being on the same order as the upper critical field

H_{c2}. If these layers surrounded paramagnetic inclusions, the magnetic response would be enhanced by the trapped vortex field and in fact could even be saturated. This would result in the FCM having a spontaneous positive magnetization behavior. In addition, one would expect little or no magnetic field dependence since the vortex field is only dependent upon superconducting parameters like the penetration depth and coherence length and not the applied magnetic field. The field dependence observed in the ZFCM can be understood in a similar manner as once the lower critical field is exceeded, magnetic vortices can be penetrate into the superconductor and become trapped at the sites of the paramagnetic inclusions. Since the number of vortices generated is related to the magnetic field strength, one would expect a field dependence for the ZFCM as shown in Figs. 5-9 to 5-11. Nevertheless, the lack of even a diamagnetic-like deviation in the ZFCM is disconcerting if this transition is truly superconducting in nature. We should point out, however, that the ZFCM for one sample did show a diamagnetic deviation at 336 K while the FCM was essentially featureless in this temperature range. Also the appearance of a positive FCM response has been observed in bulk superconductors, the so-called paramagnetic Meissner effect.[20,21] Clearly more work is required to fully understand the nature of this transition from a magnetic perspective as well as to clarify the exact synthesis conditions.

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LIST OF FIGURES

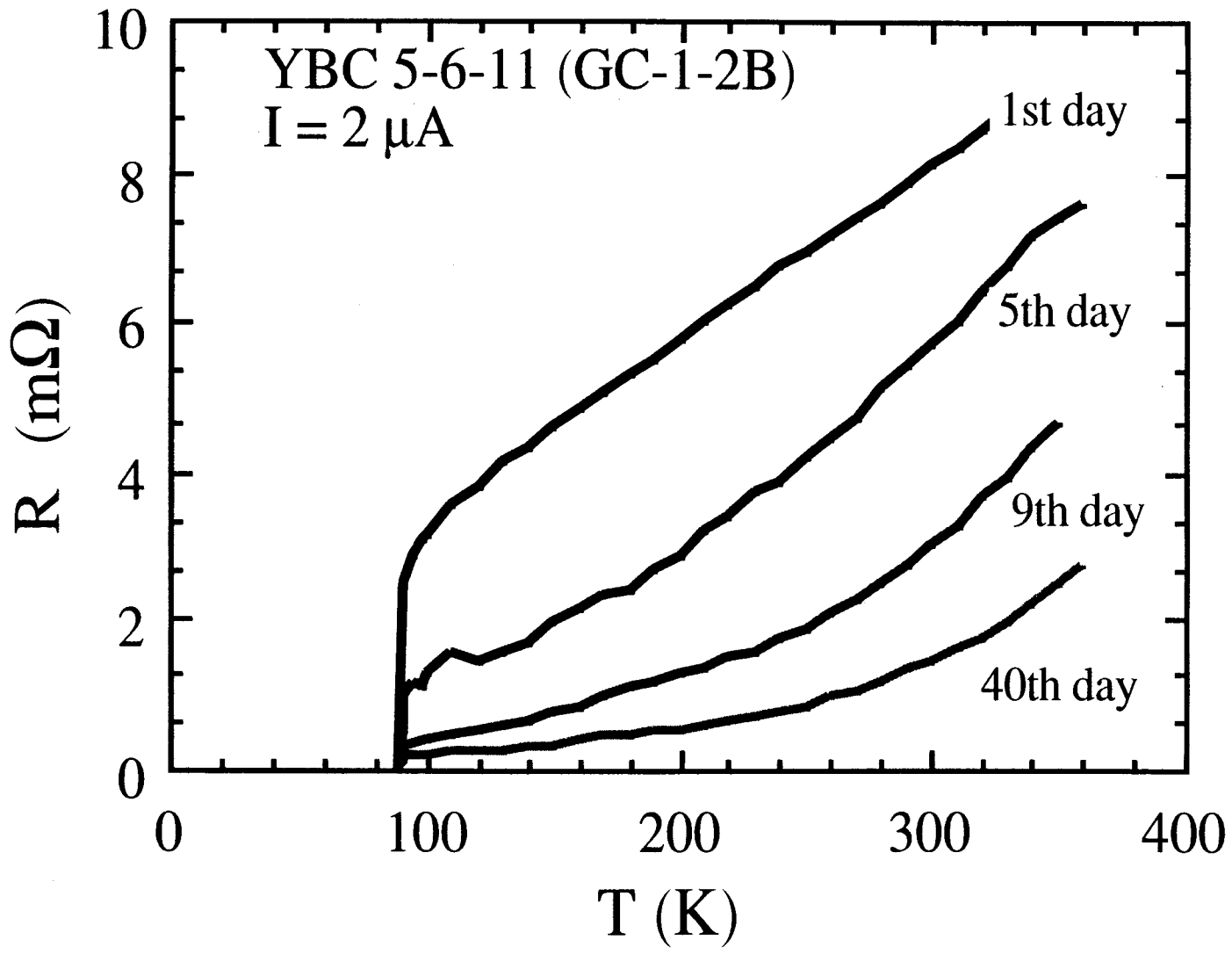

Fig. 3-1. The time dependence of the resistance for a nominal 5:6:11 YBaCuO multi-phase ceramic sample in 2 atm of O_2 gas as a function of temperature.

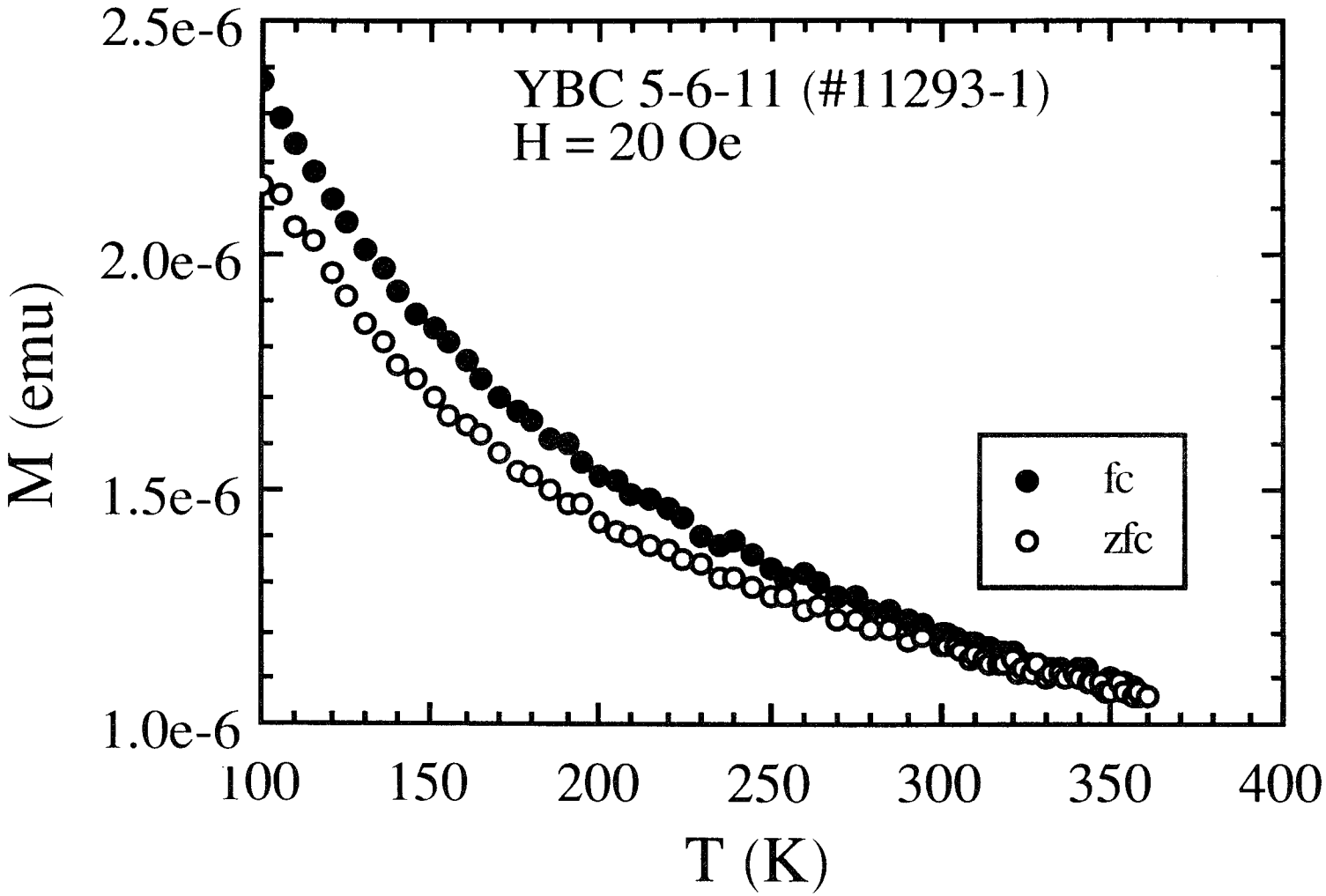

Fig. 3-2. The ZFCM and FCM for a multi-phase YBaCuO sample of nominal composition 5:6:11.

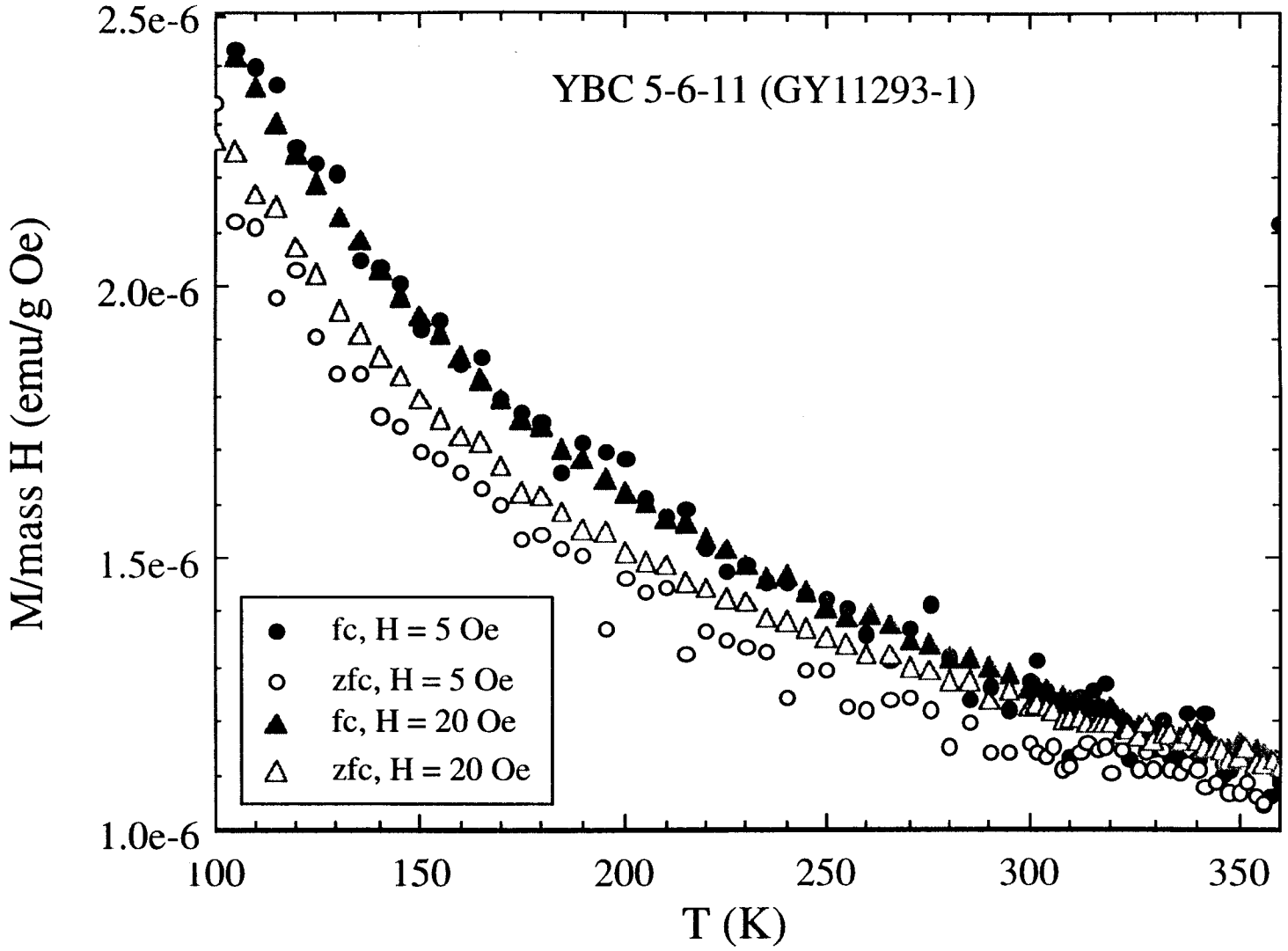

Fig. 3-3. The ZFCM and FCM for a ceramic 5:6:11 YBaCuO sample (11293-1) for two different magnetic fields.

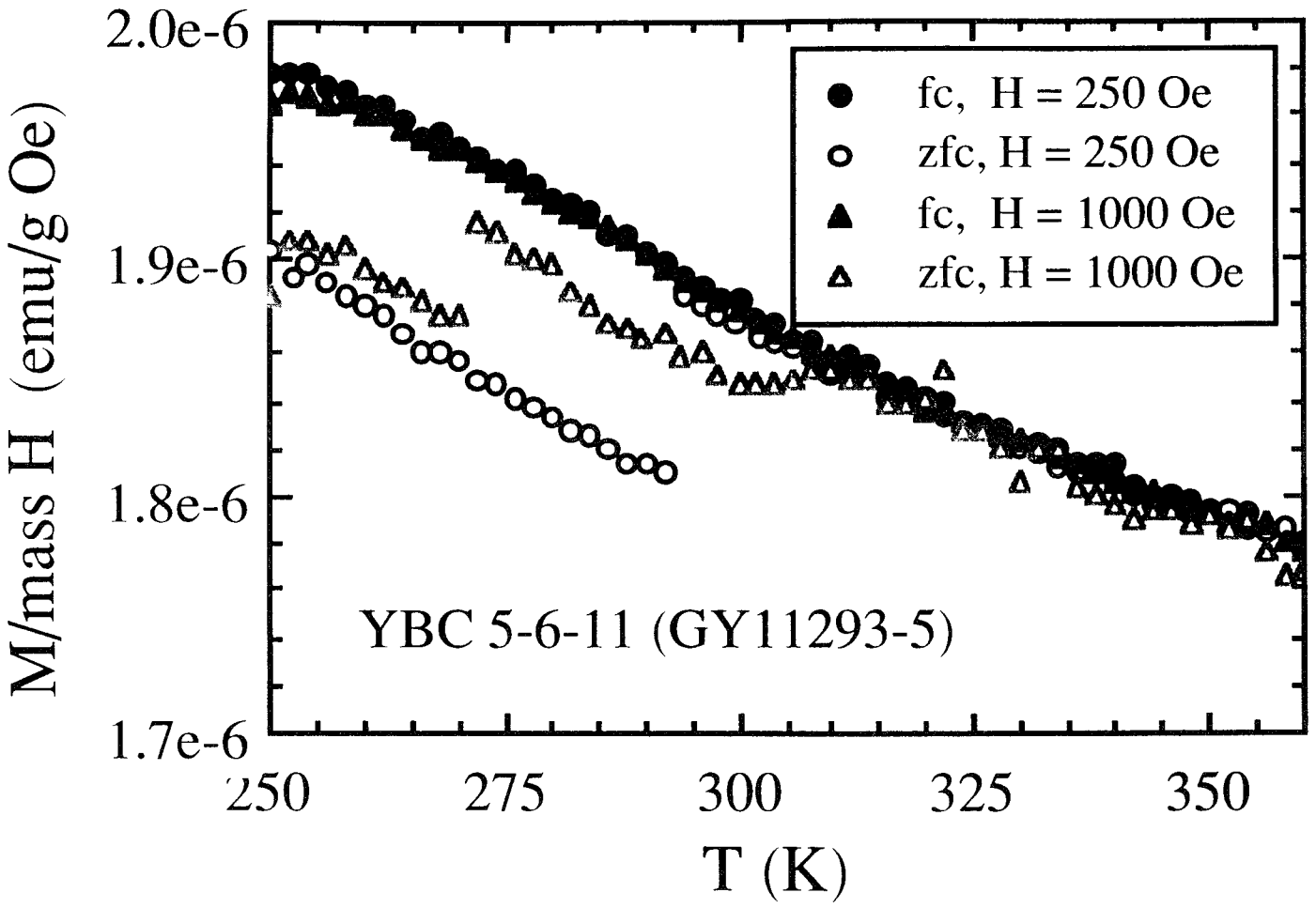

Fig. 3-4. The ZFCM and FCM for a ceramic 5:6:11 YBaCuO sample for two different fields, 250 Oe and 1000 Oe. Note that the flux jumps as well as the diamagnetic-like deviations at 310 K.

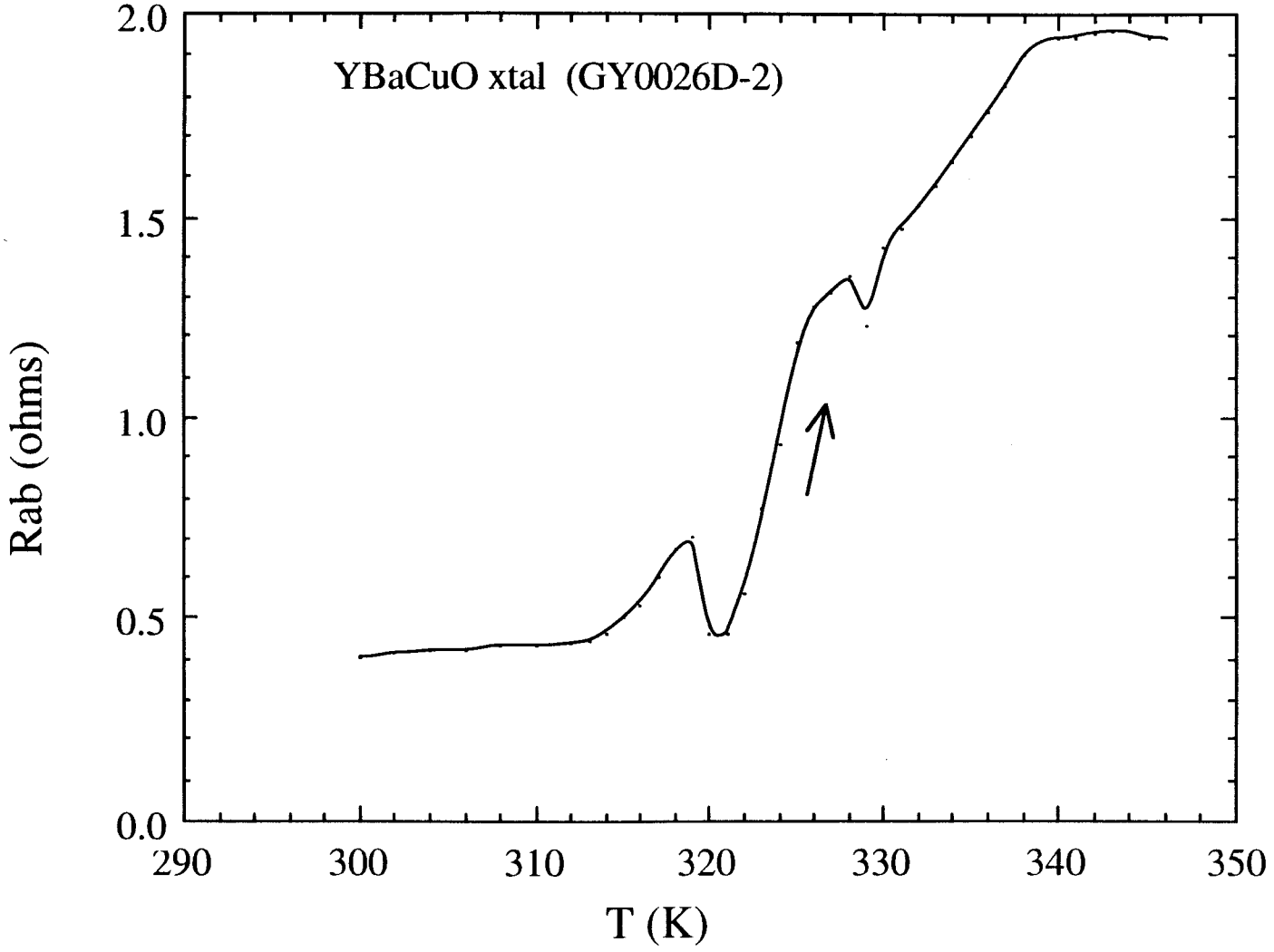

Fig. 4-1. Resistance along *ab*-plane of a nominal $YBa_2Cu_3O_{7-\delta}$ single crystal showing a resistive transition in the vicinity of 340 K.

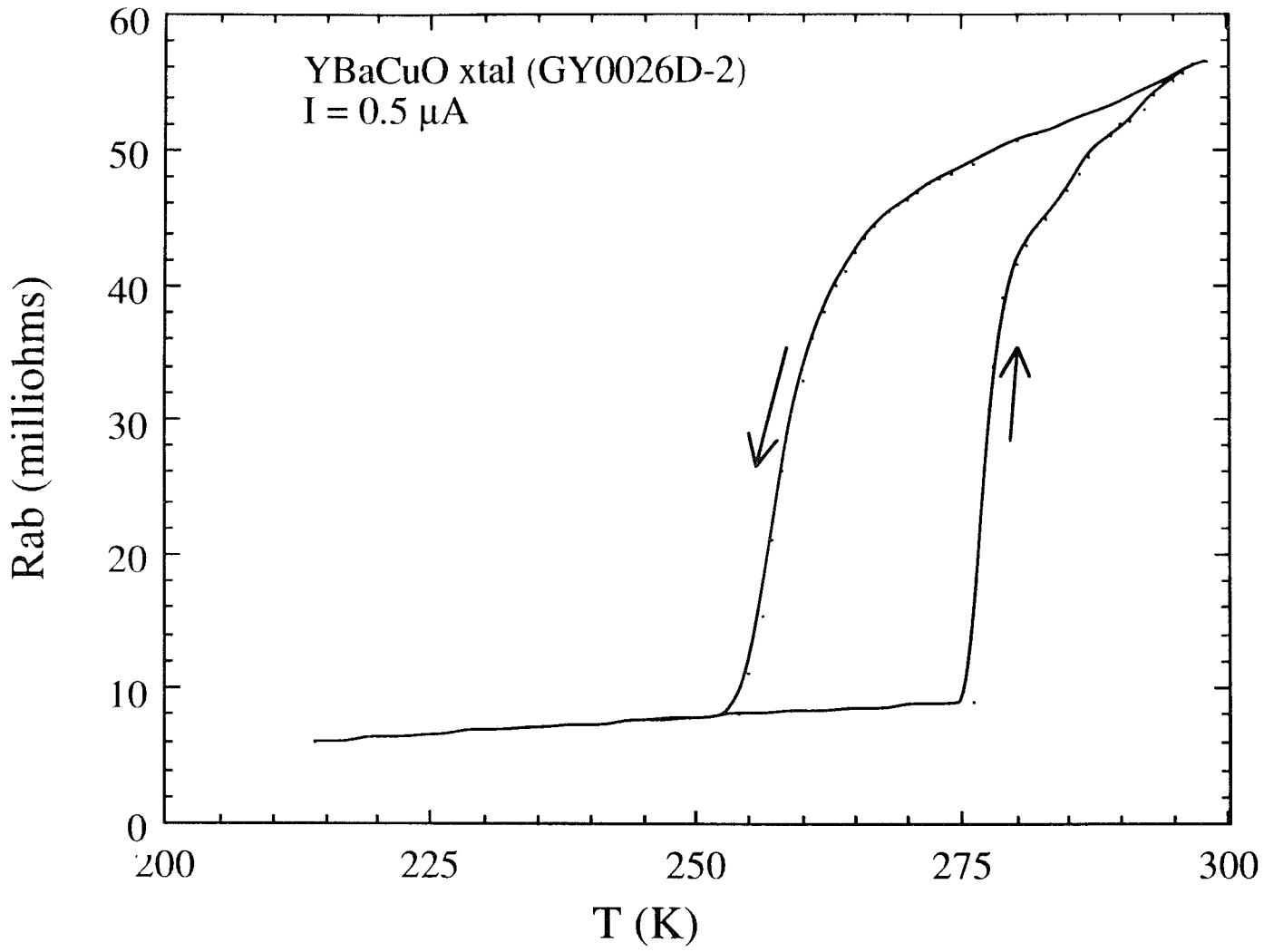

Fig. 4-2. Resistance along *ab*-plane of a nominal $YBa_2Cu_3O_{7-\delta}$ single crystal showing a hysteretic behavior in the resistive transition below 280 K.

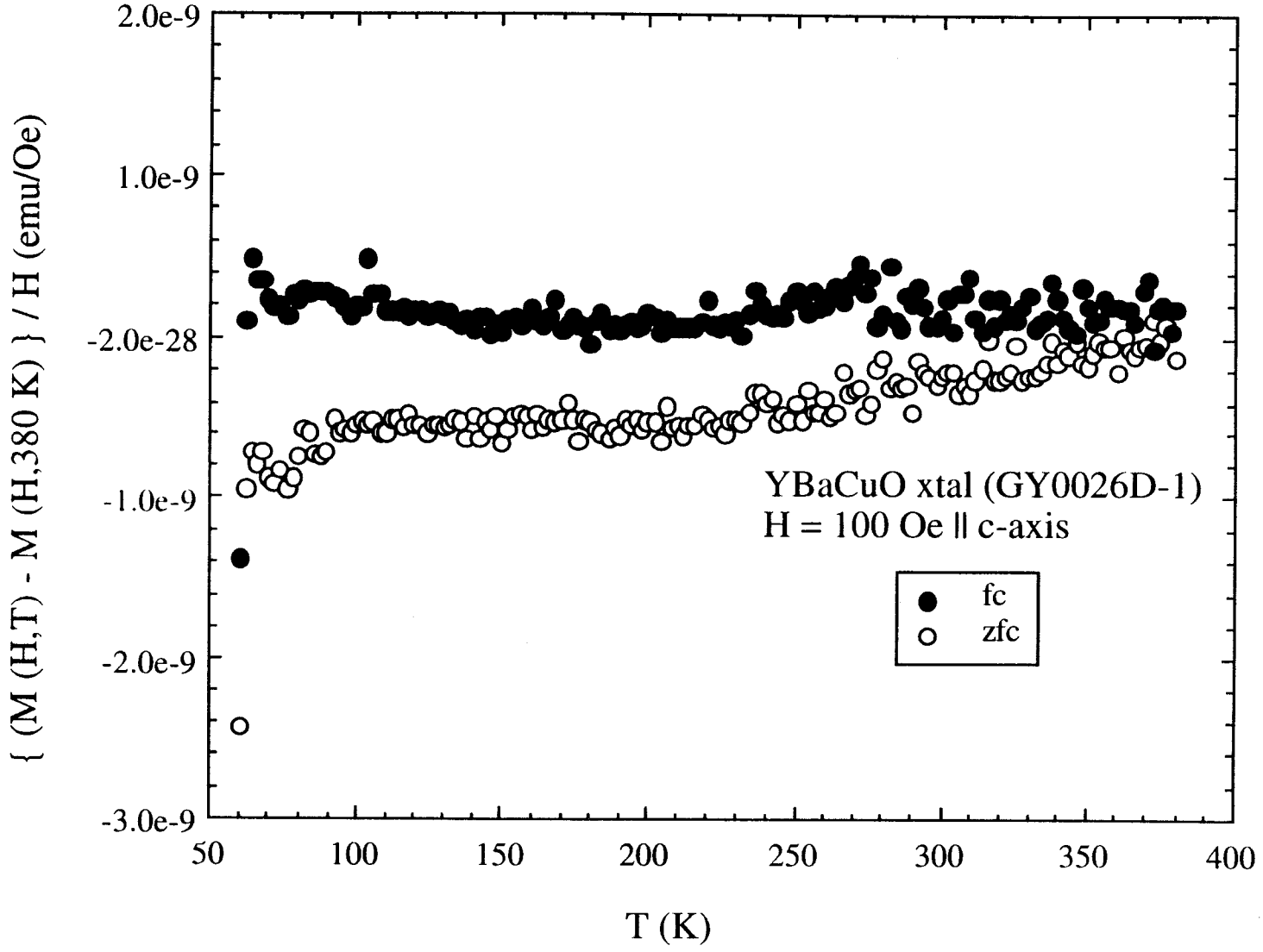

Fig. 4-3. The ZFCM and FCM for a nominal $YBa_2Cu_3O_{7-\delta}$ single crystal sample (GY0026D-1) in a field of 100 Oe.

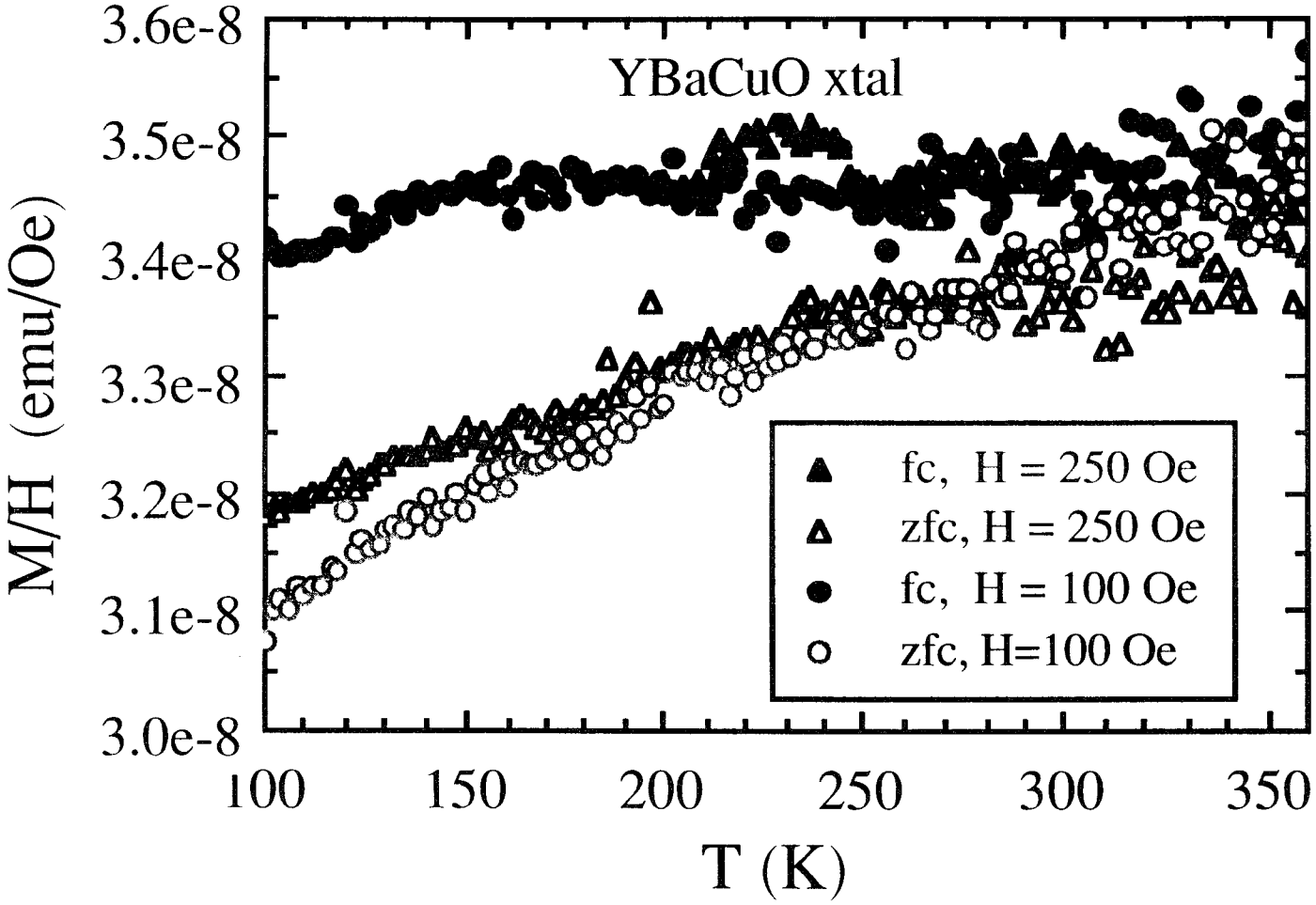

Fig. 4-4. The ZFCM and FCM for a nominal $YBa_2Cu_3O_{7-\delta}$ single crystal sample (91093-4) in fields of 100 Oe and 250 Oe.

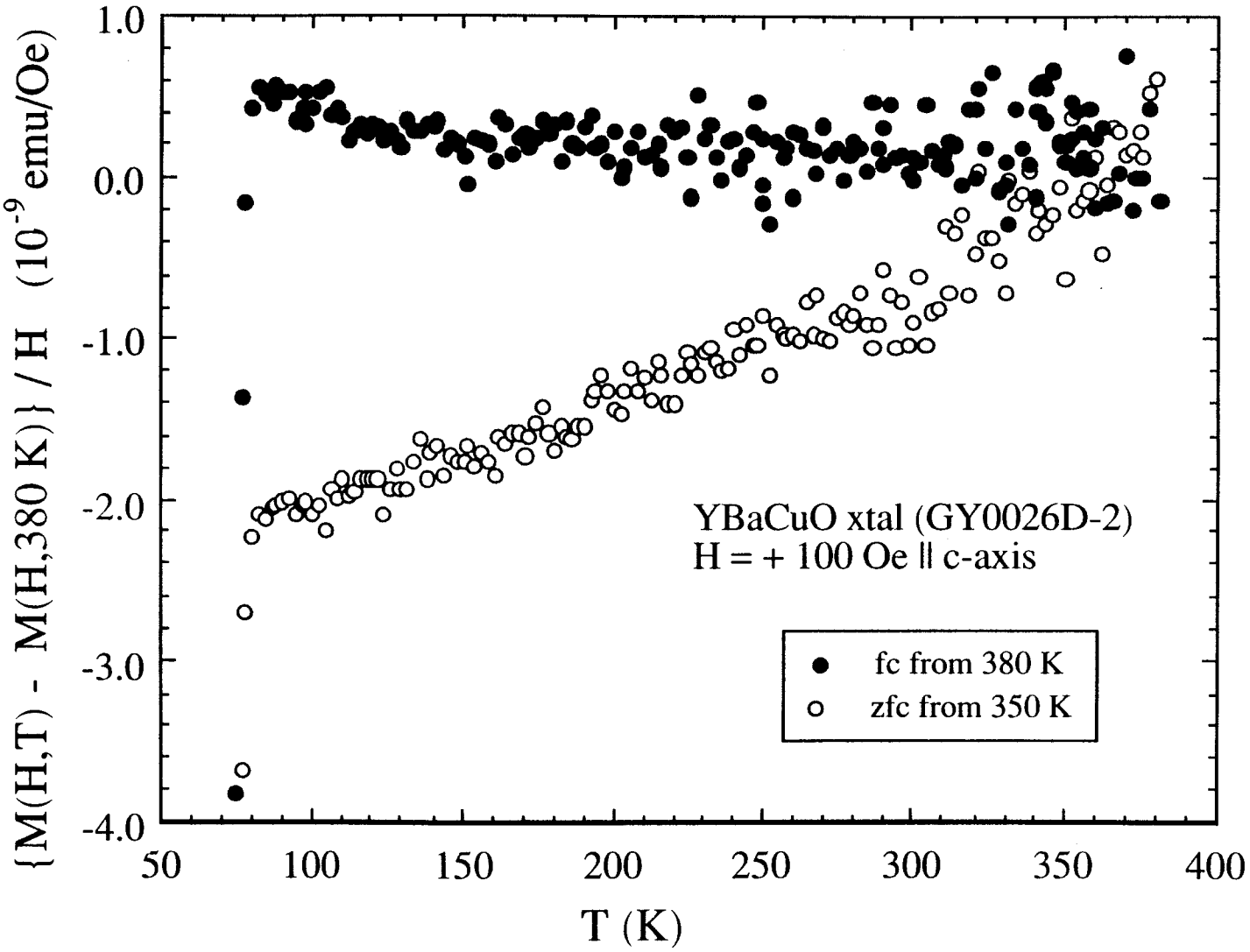

Fig. 4-5. The ZFCM and FCM for a nominal $YBa_2Cu_3O_{7-\delta}$ single crystalsample (GY0026D-2) in a field of 100 Oe.

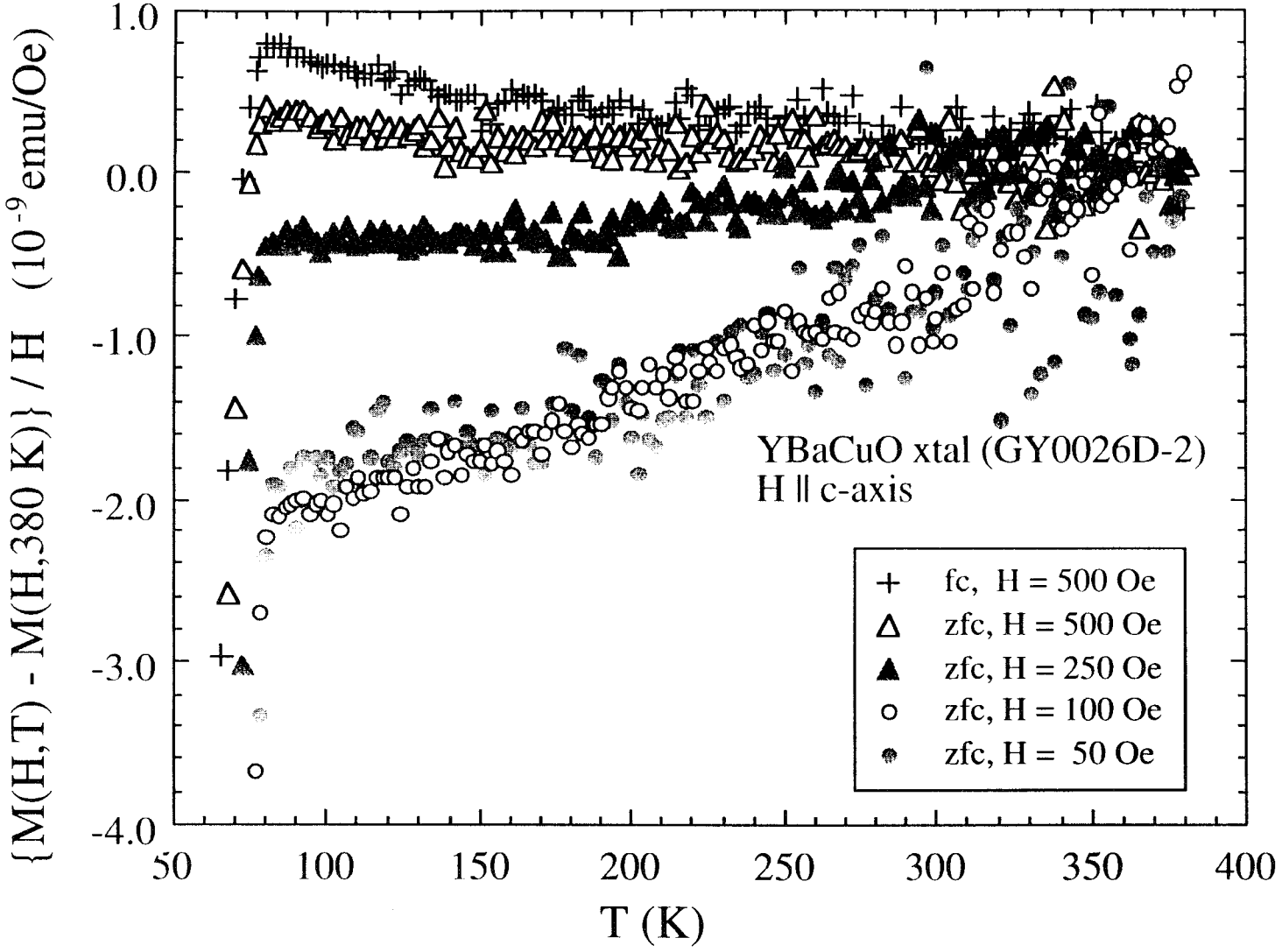

Fig. 4-6. The magnetic field of the ZFCM for a nominal $YBa_2Cu_3O_{7-\delta}$ single crystal sample (GY0026D-2).

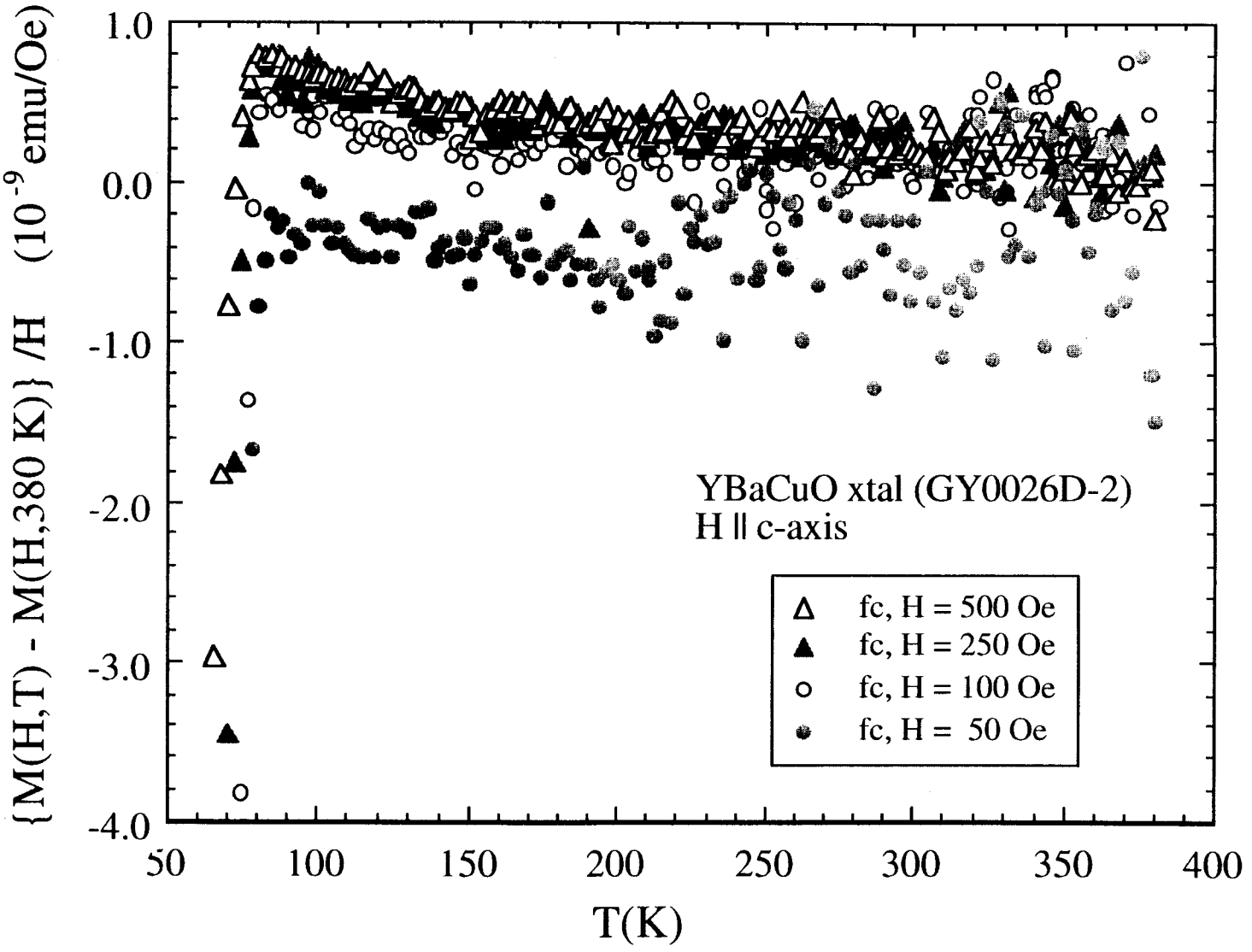

Fig 4-7 The magnetic field of the FCM for a nominal $YBa_2Cu_3O_{7-\delta}$ single crystal sample (GY0026D-2).

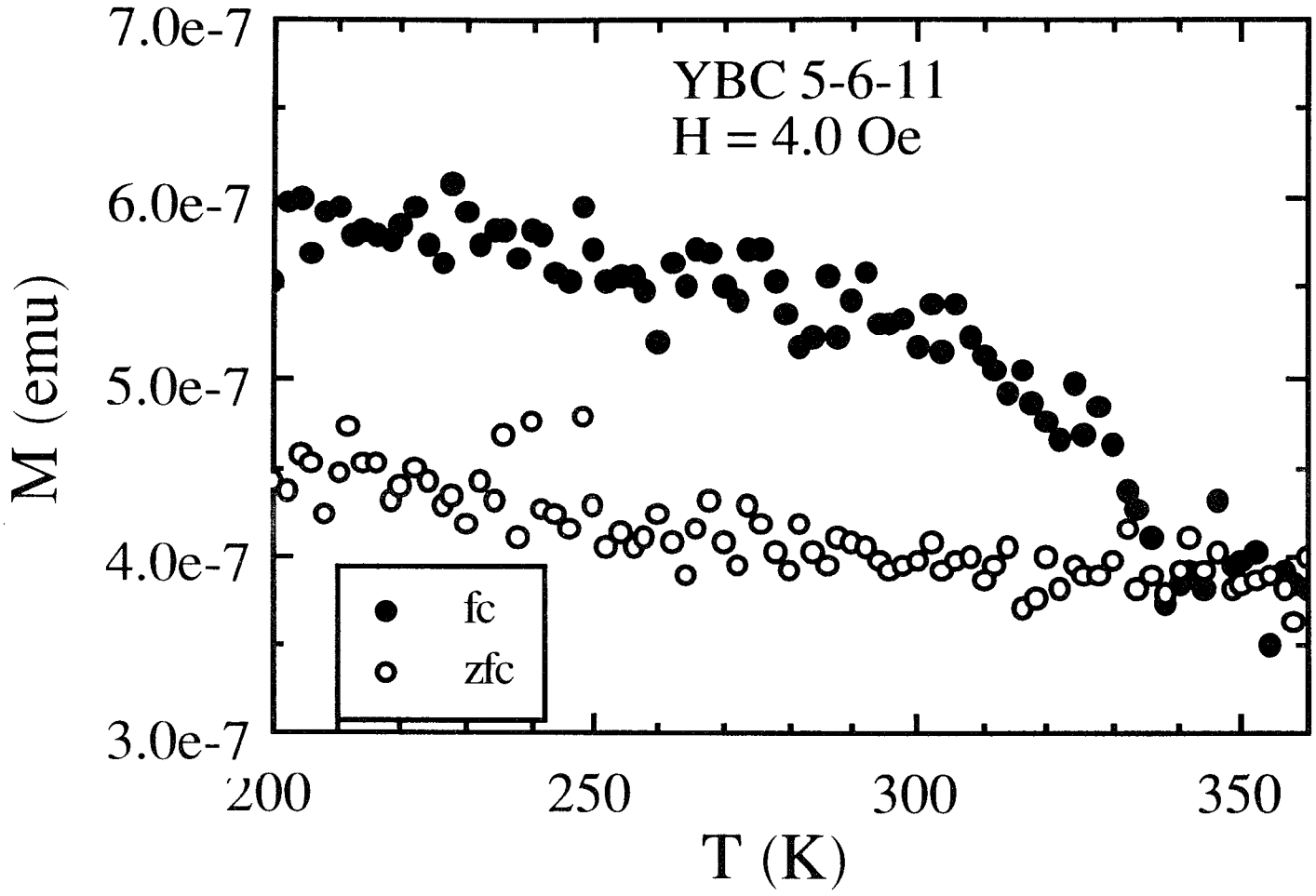

Fig. 5-1. The ZFCM and FCM for a nominal 5:6:11 YBaCuO sample which exhibits a 336-K transition.

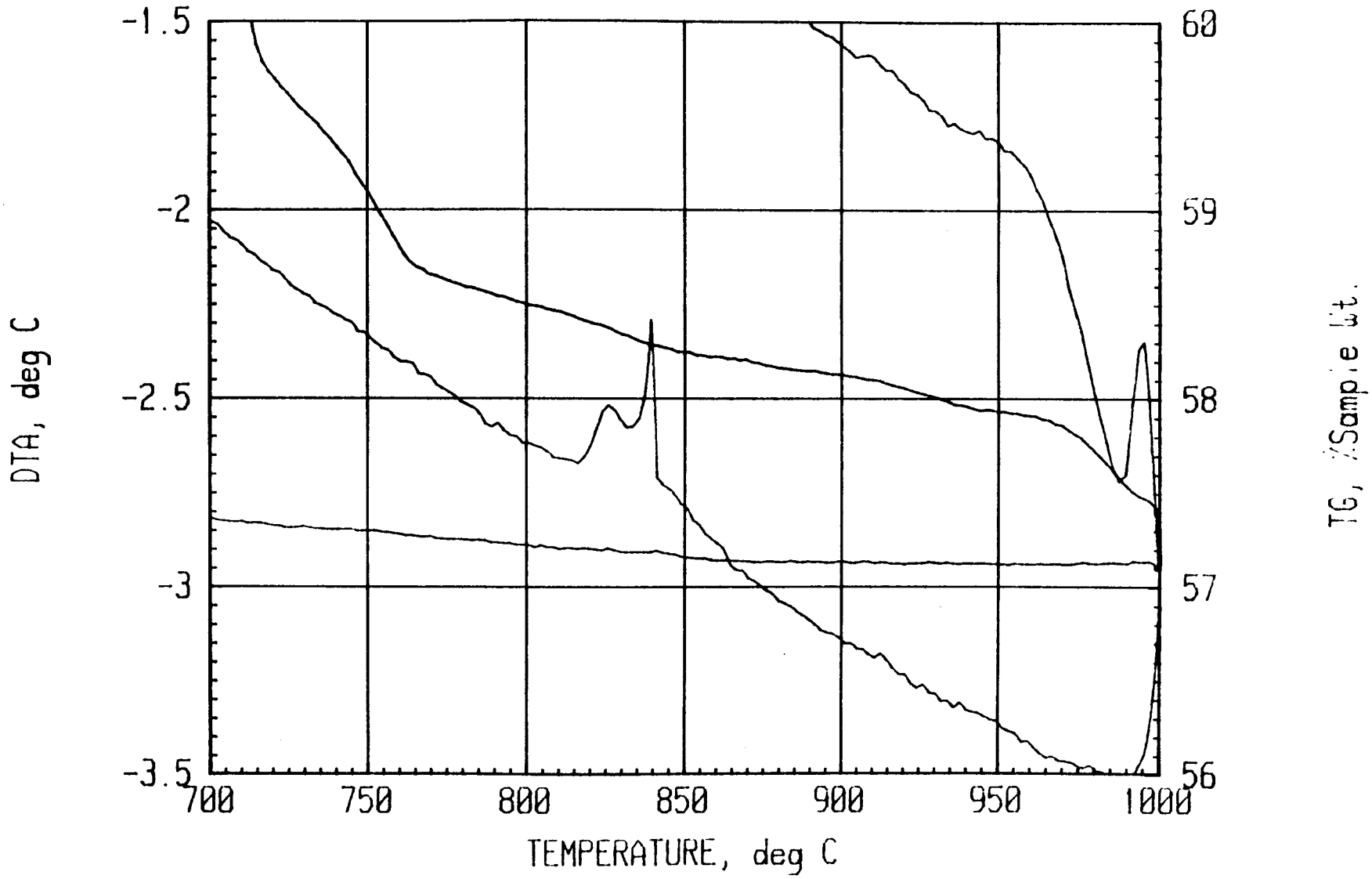

Fig. 5-2. Simultaneous DTA/TG data during the warming and cooling cycles of the synthesis of a nominal 1 : 2 : 2.75 YBaCuO sample in Ar gas.

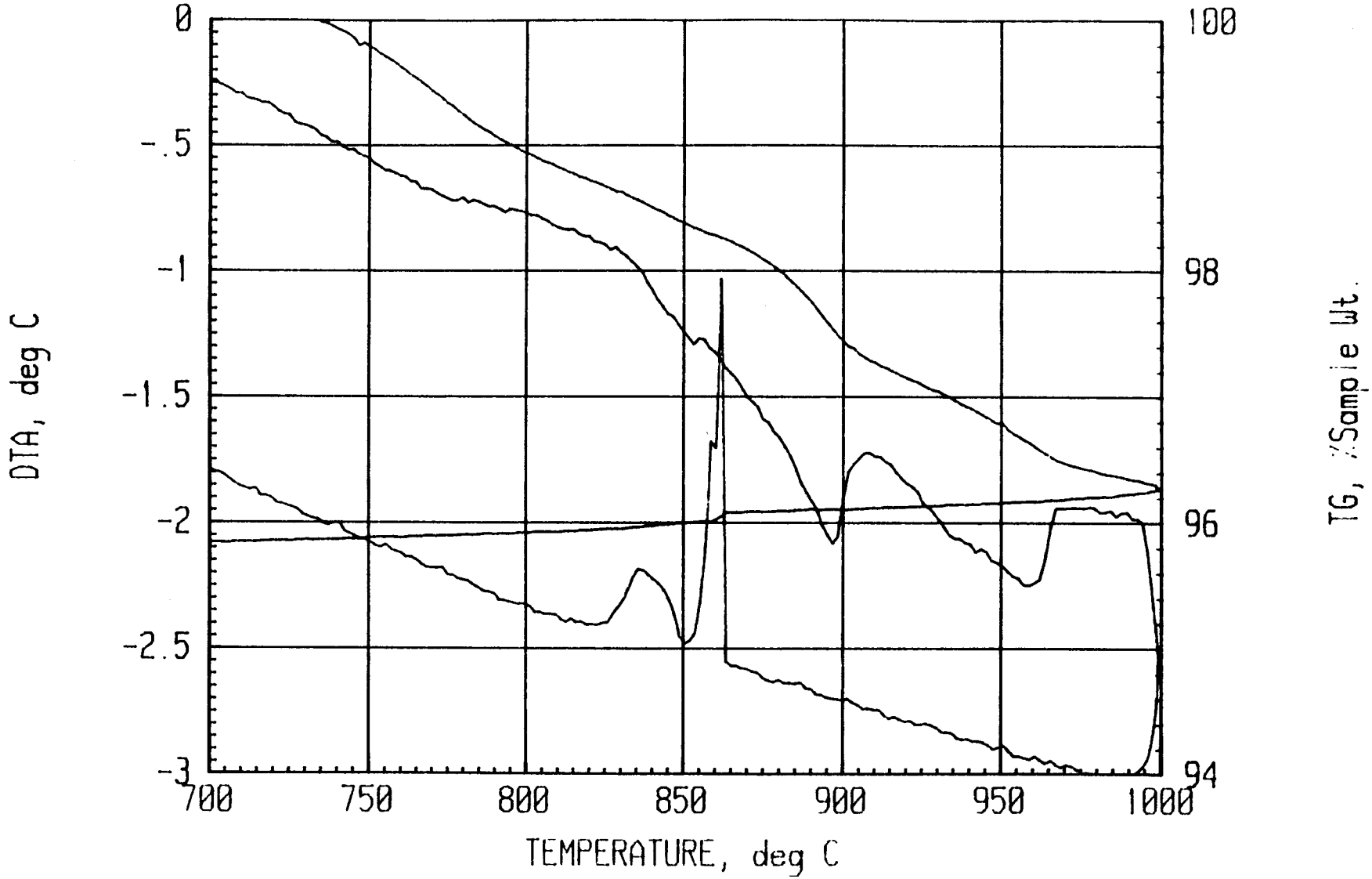

Fig. 5-3. Simultaneous DTA/TG data during the warming and cooling cycles of the synthesis of a nominal 1 : 2 : 4 YBaCuO sample in Ar gas.

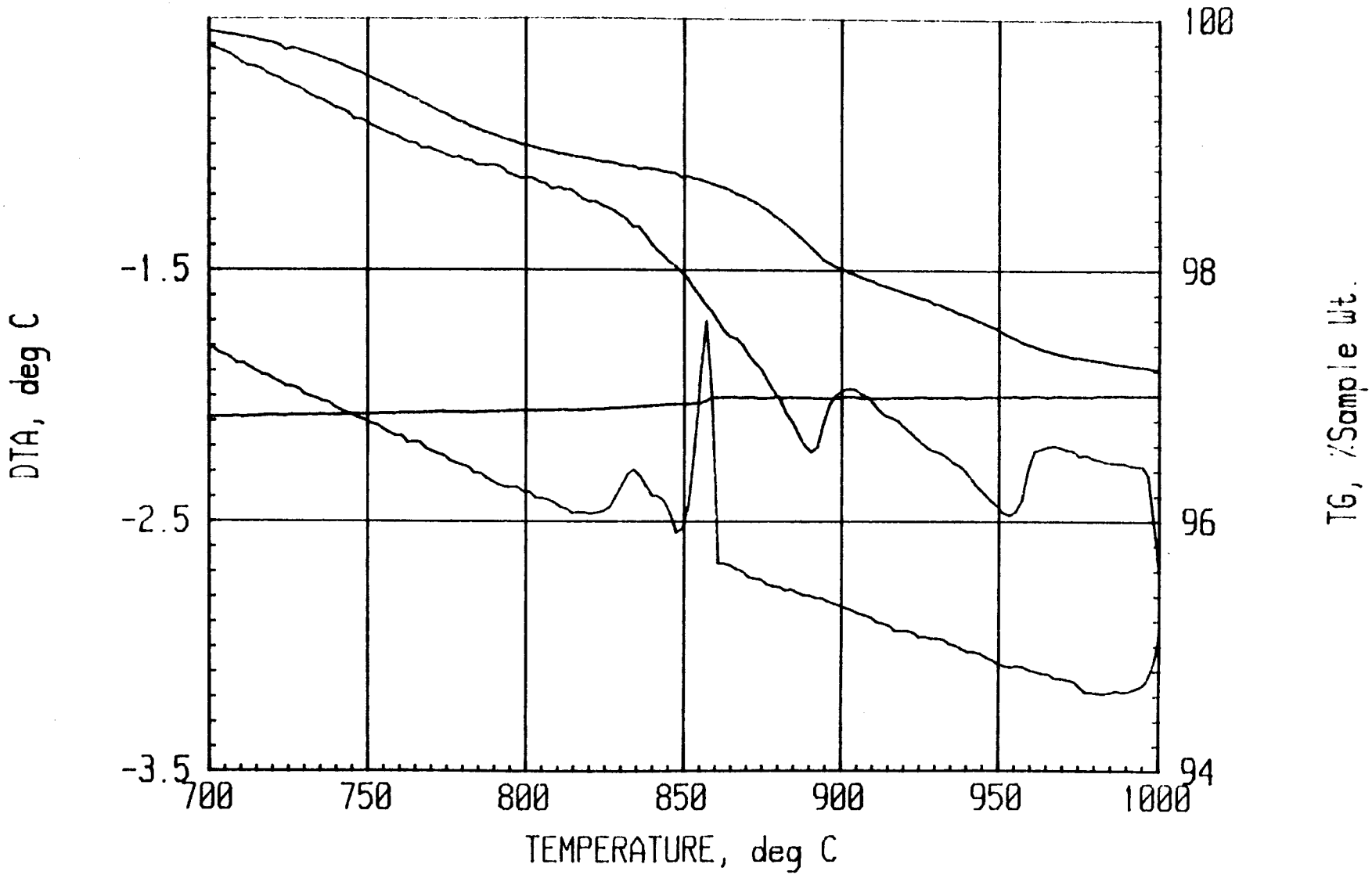

Fig. 5-4. Simultaneous DTA/TG data during the warming and cooling cycles of the synthesis of a nominal 4 : 5 : 9 YBaCuO sample in Ar gas.

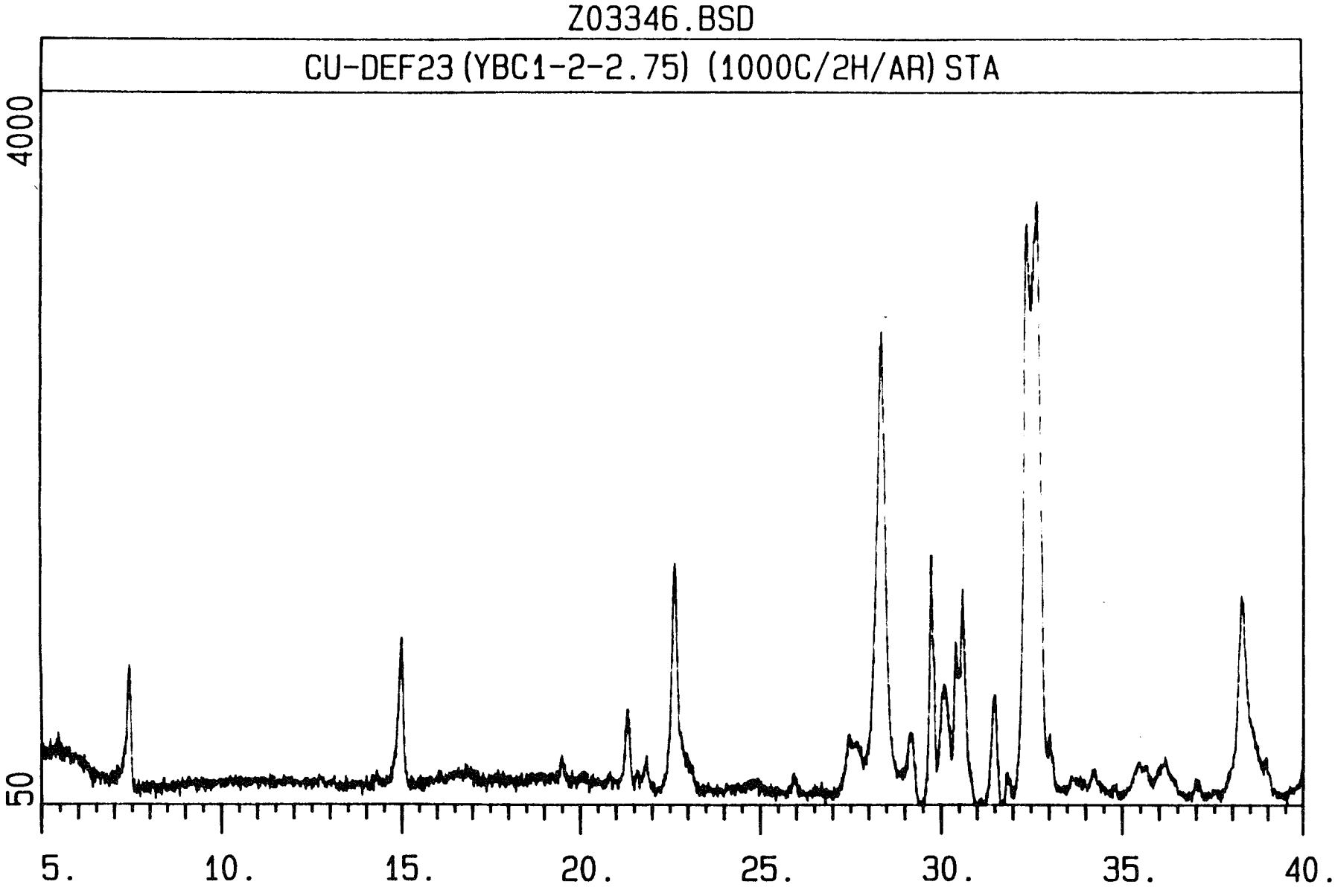

Fig. 5-5. X-ray diffraction pattern for a nominal 1 : 2 : 2.75 YBaCuO sample synthesized at 1000°C in Ar.

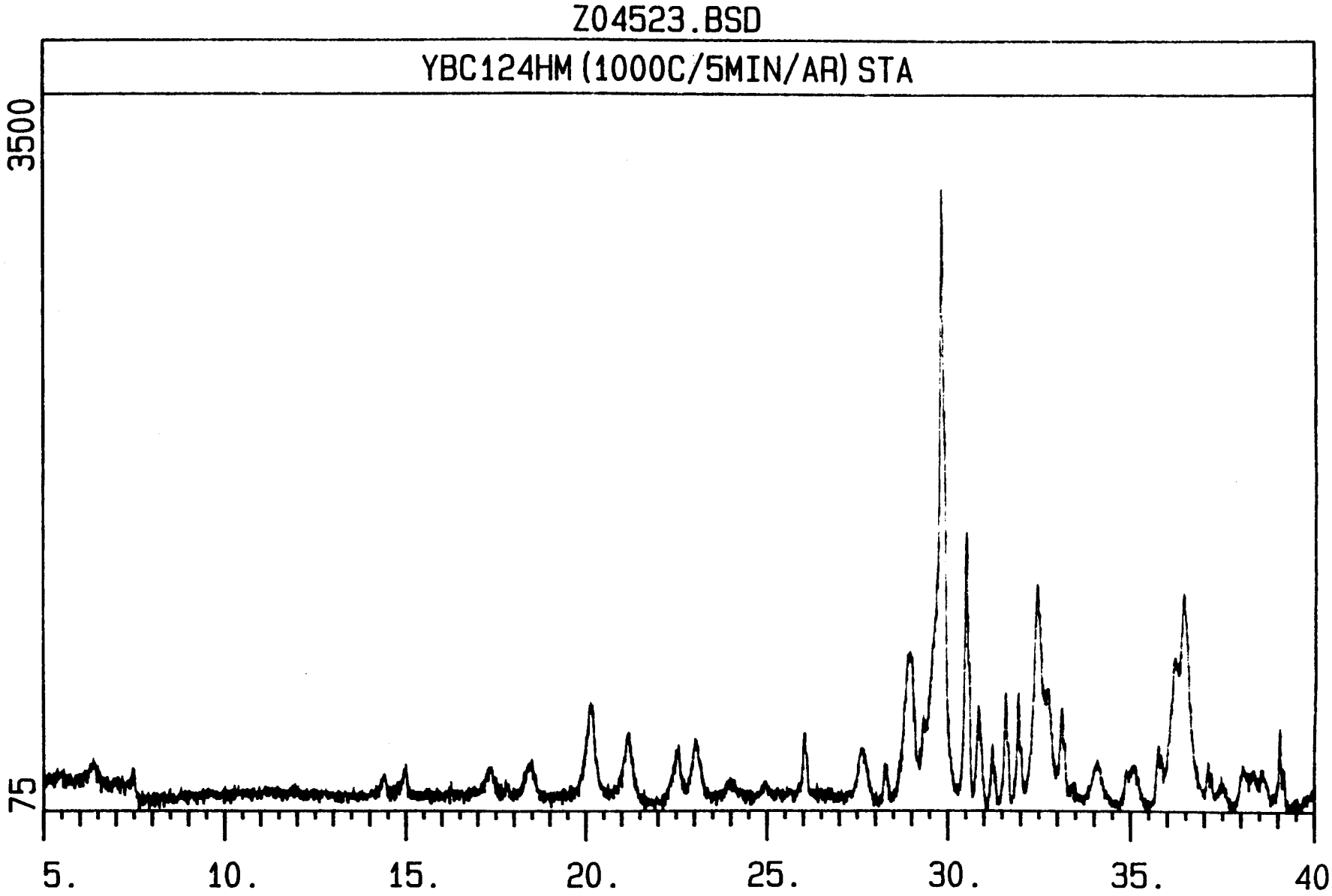

Fig. 5-6. X-ray diffraction pattern for a nominal 1 : 2 : 4 YBaCuO sample synthesized at 1000°C in Ar.

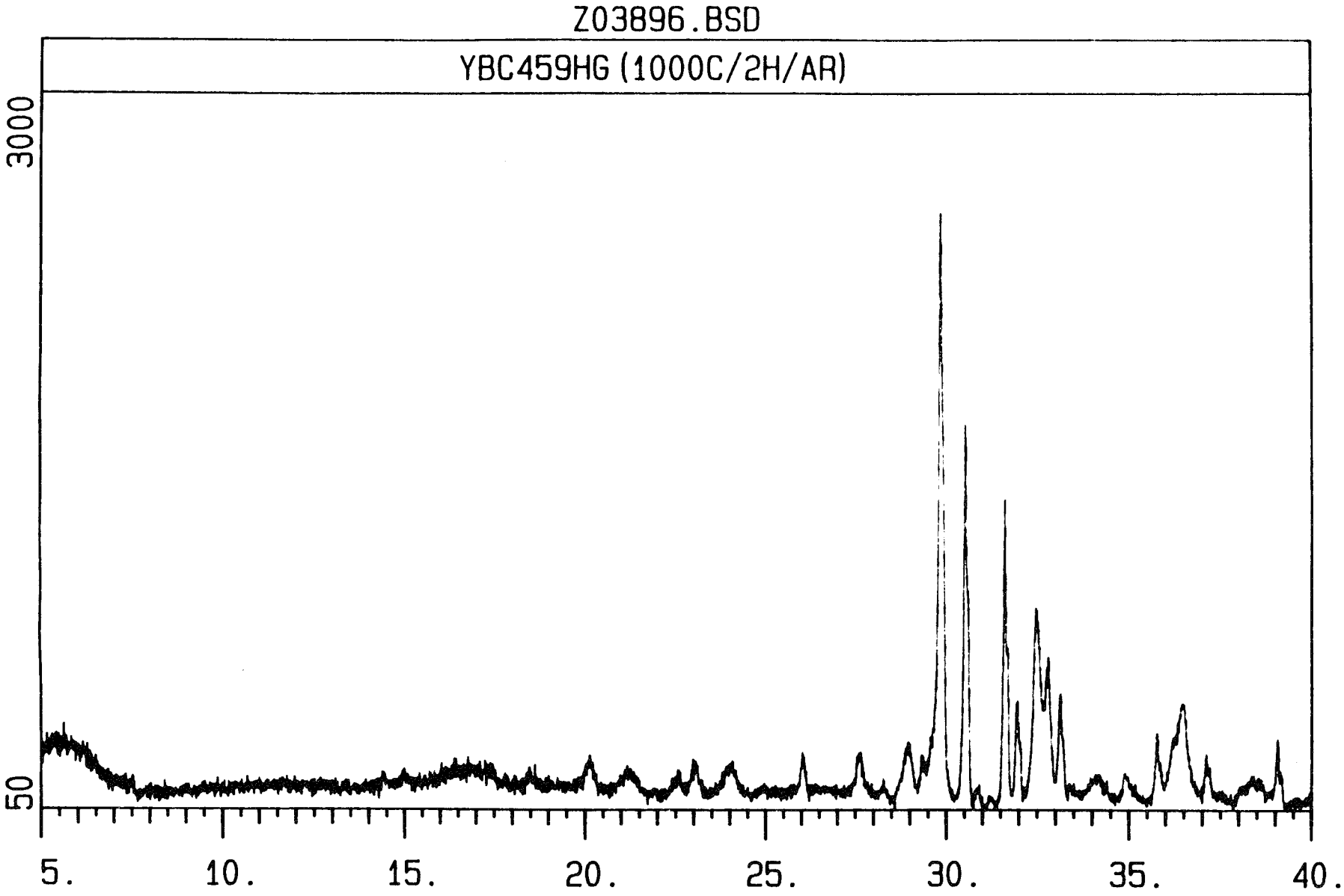

Fig. 5-7. X-ray diffraction pattern for a nominal 4 : 5 : 9 YBaCuO sample synthesized at 1000°C in Ar.

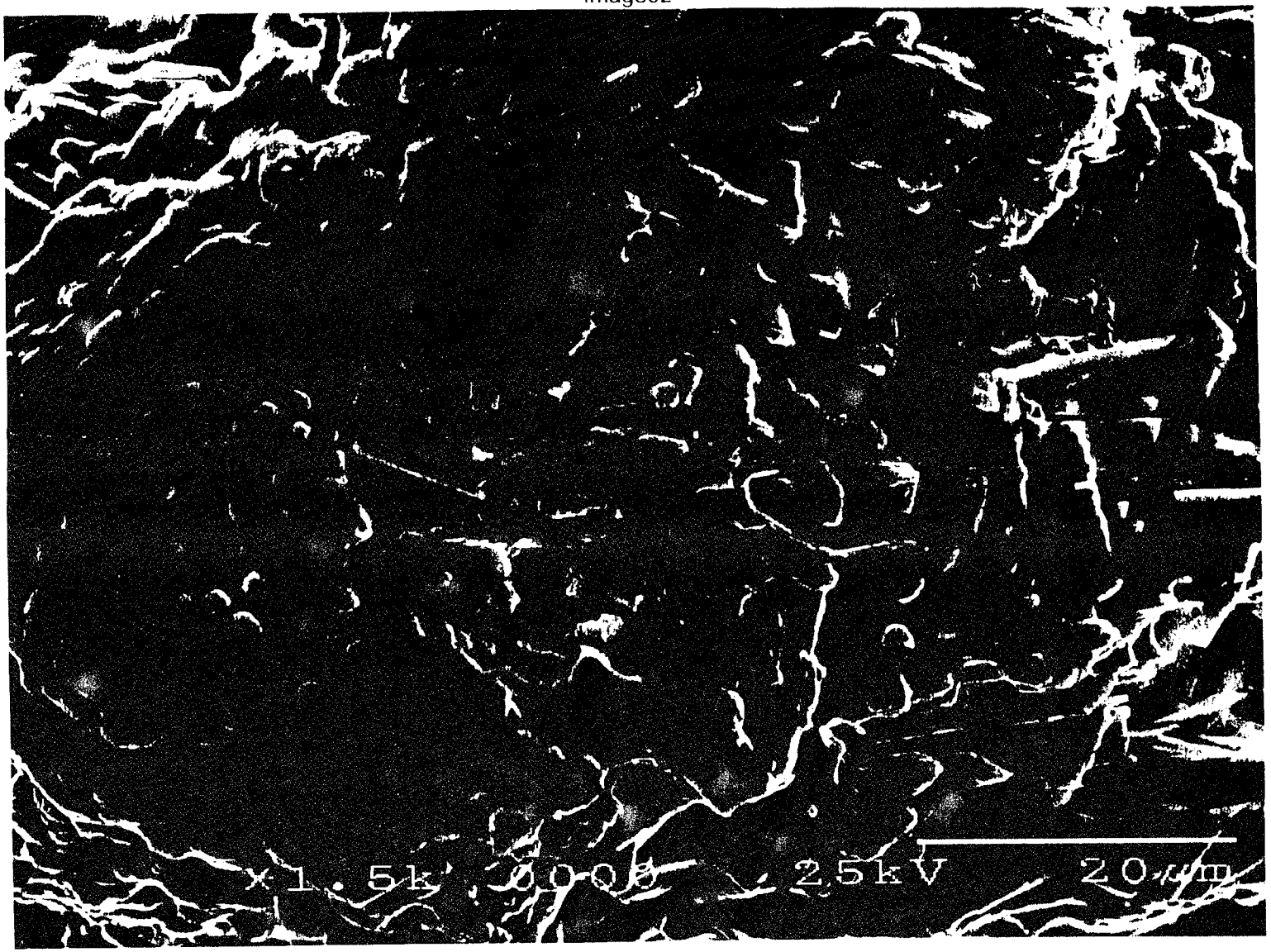

Fig. 5-8. SEM photograph for a nominal 5:6:11 YBaCuO sample exhibiting the 336-K transition.

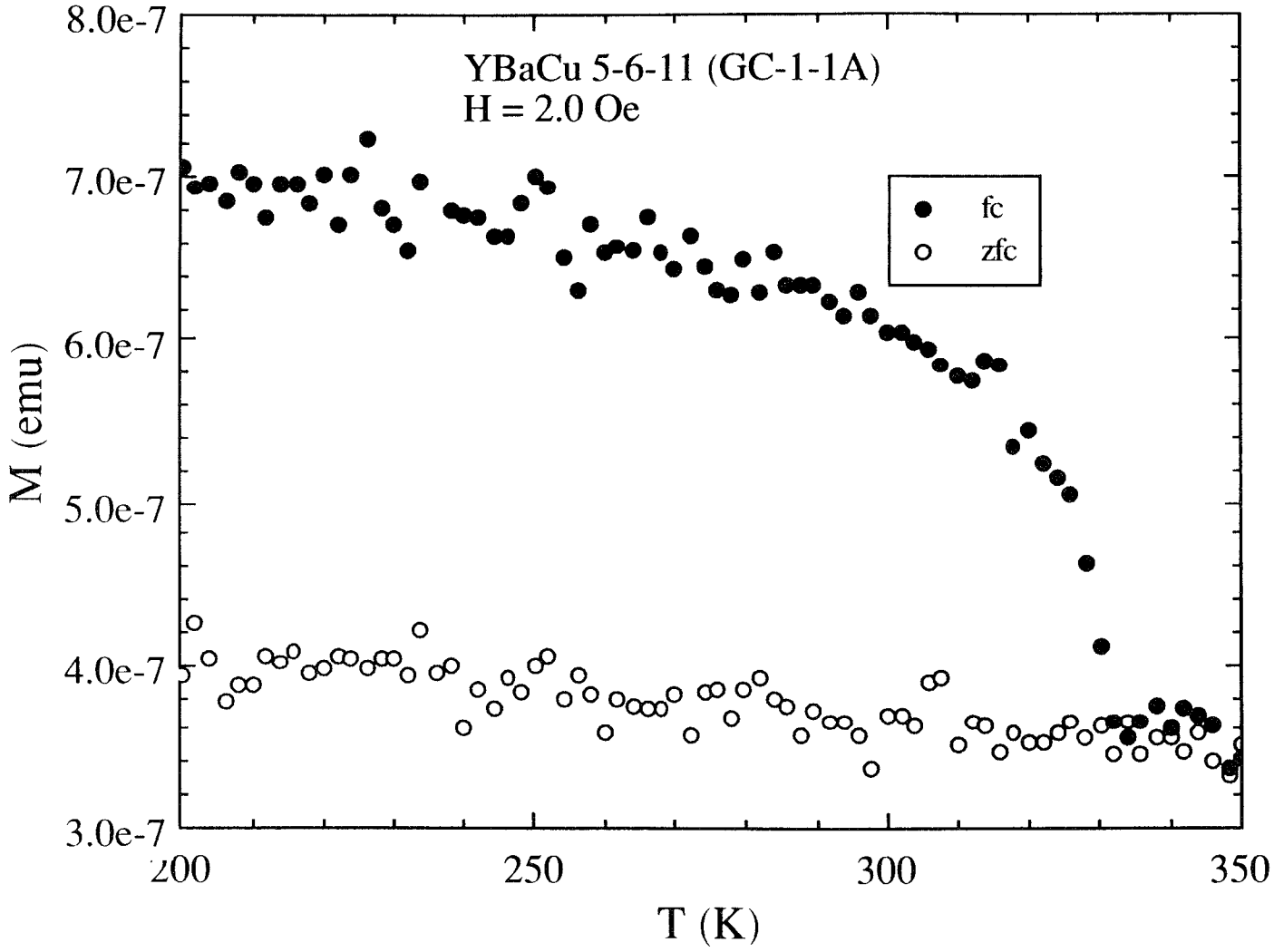

Fig. 5-9. The ZFCM and FCM for a nominal 5:6:11 YBaCuO sample (GC-1-1) for a field of 2 Oe.

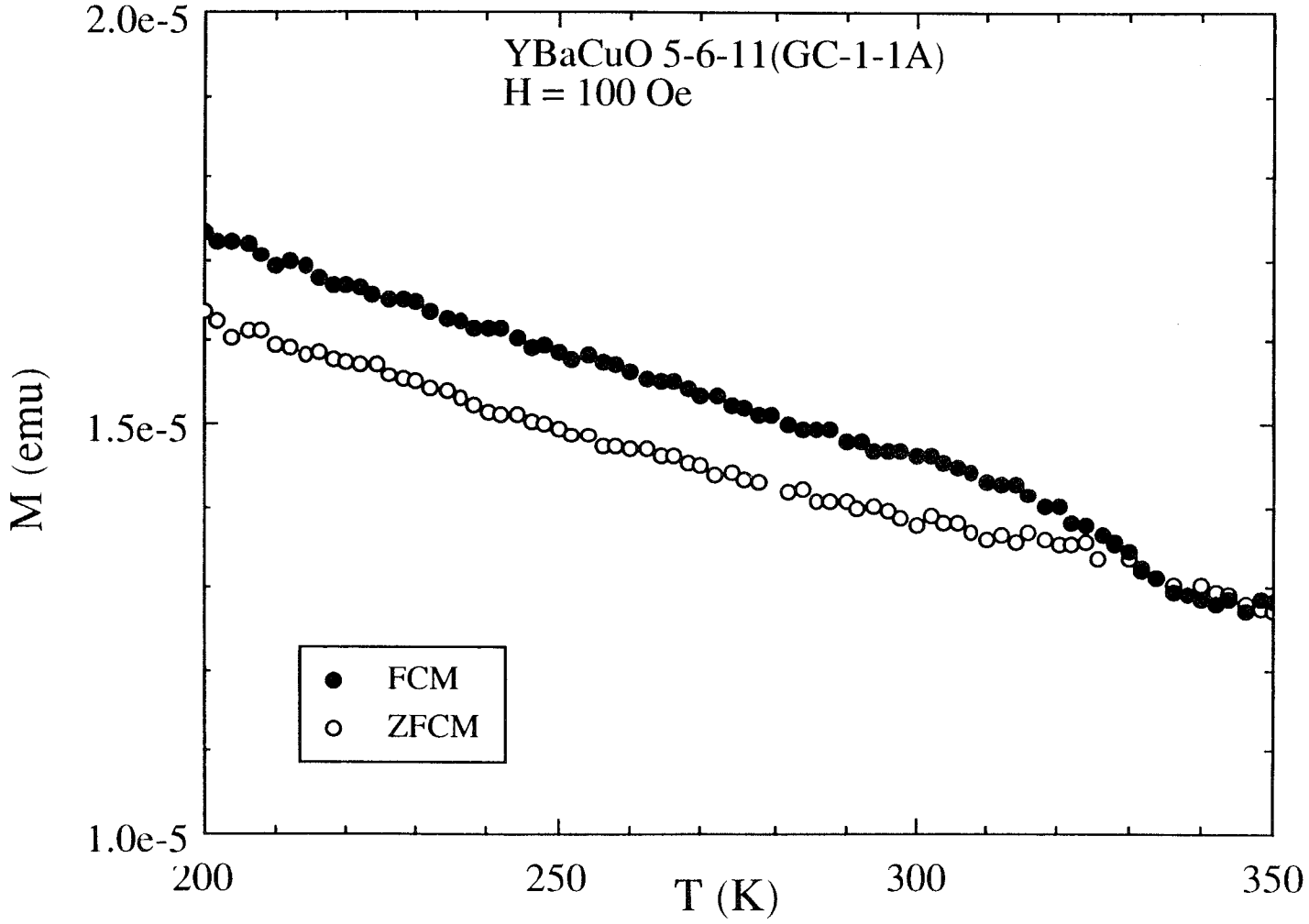

Fig. 5-10 The ZFCM and FCM for a nominal 5:6:11 YBaCuO sample (GC-1-1) for a field of 100 Oe.

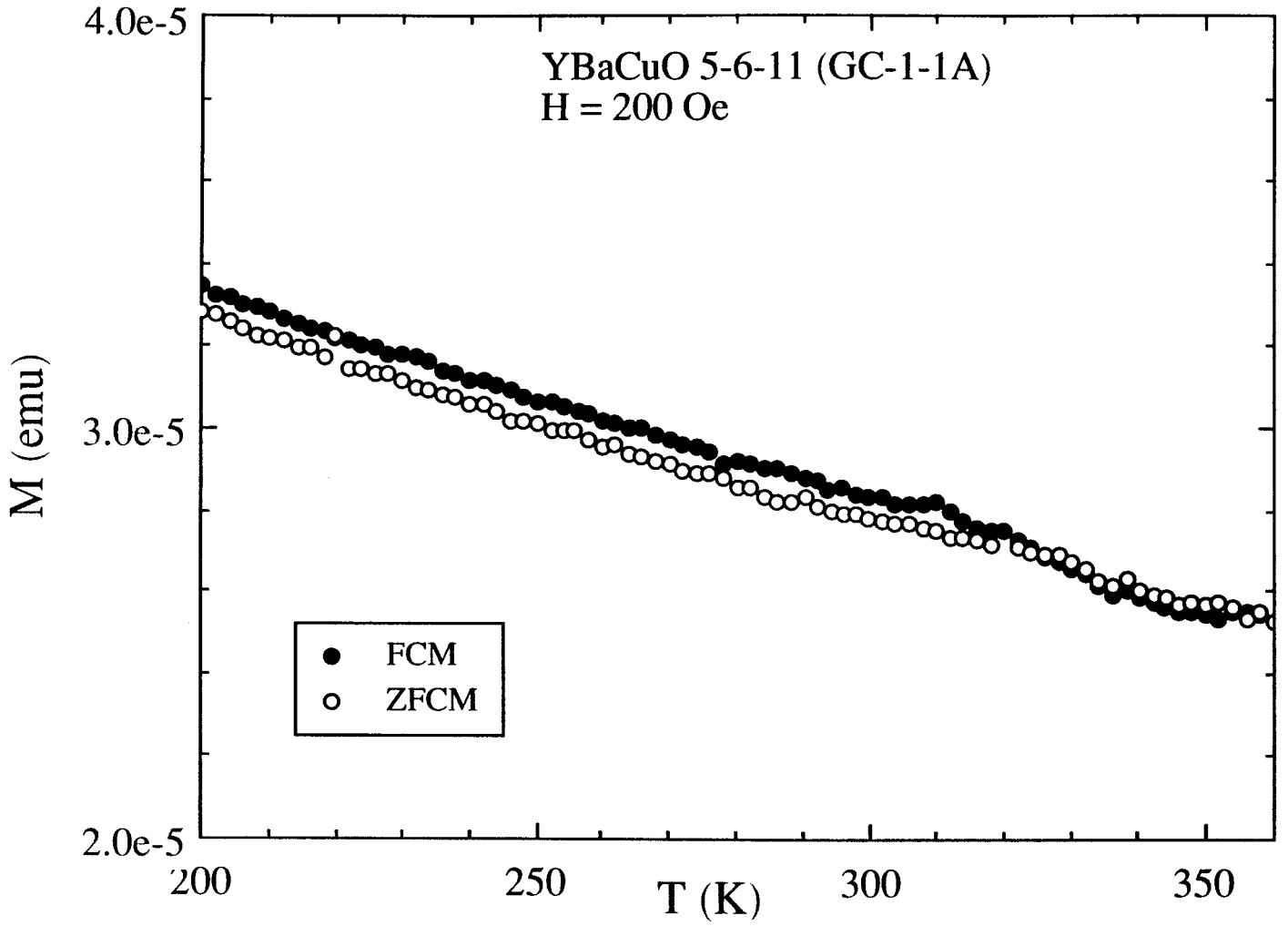

Fig. 5-11. The ZFCM and FCM for a nominal 5:6:11 YBaCuO sample (GC-1-1) for a field of 200 Oe.

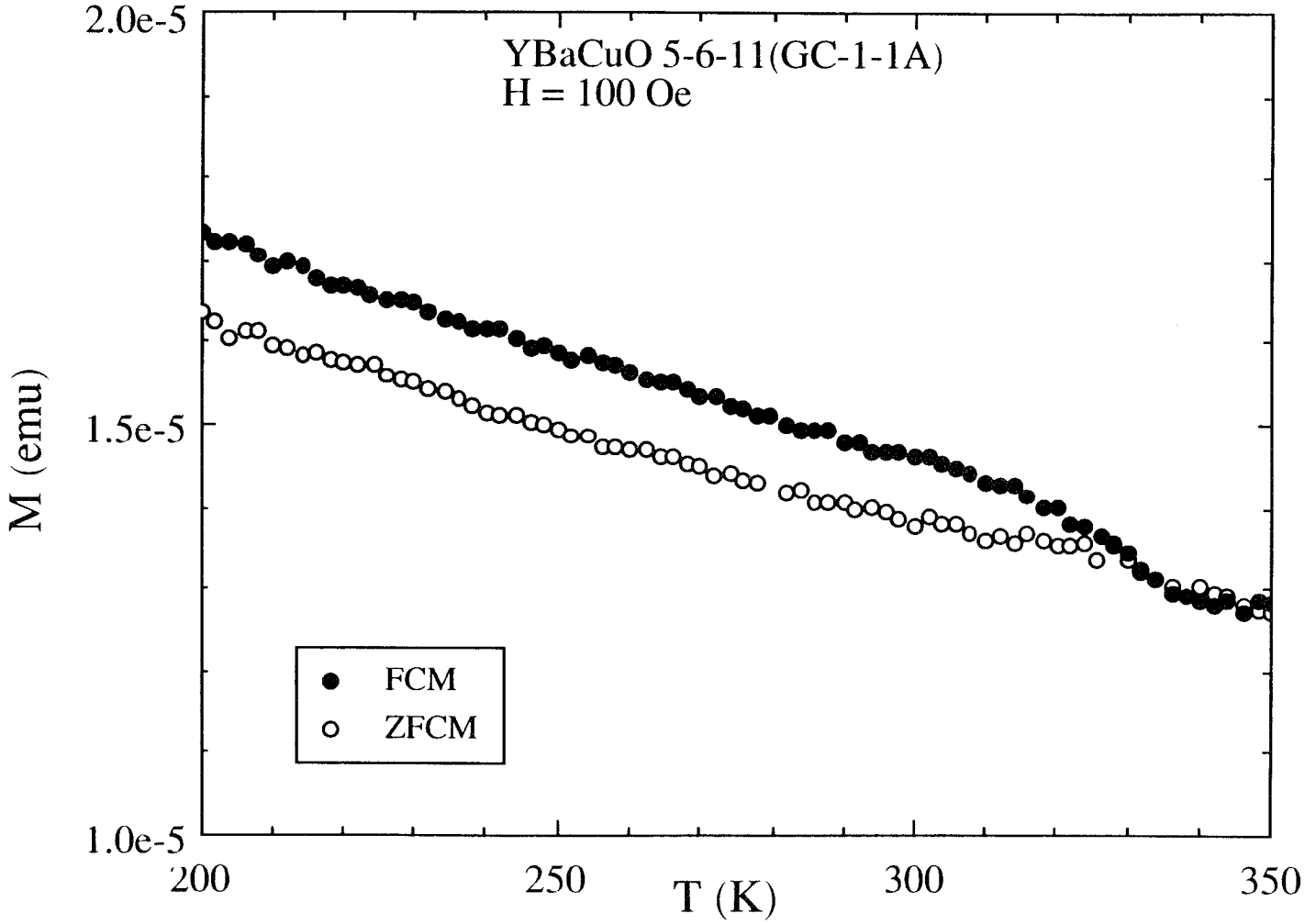

Fig 5-10 The ZFCM and FCM for a nominal 5:6:11 YBaCuO sample (GC-1-1) for a field of 100 Oe.

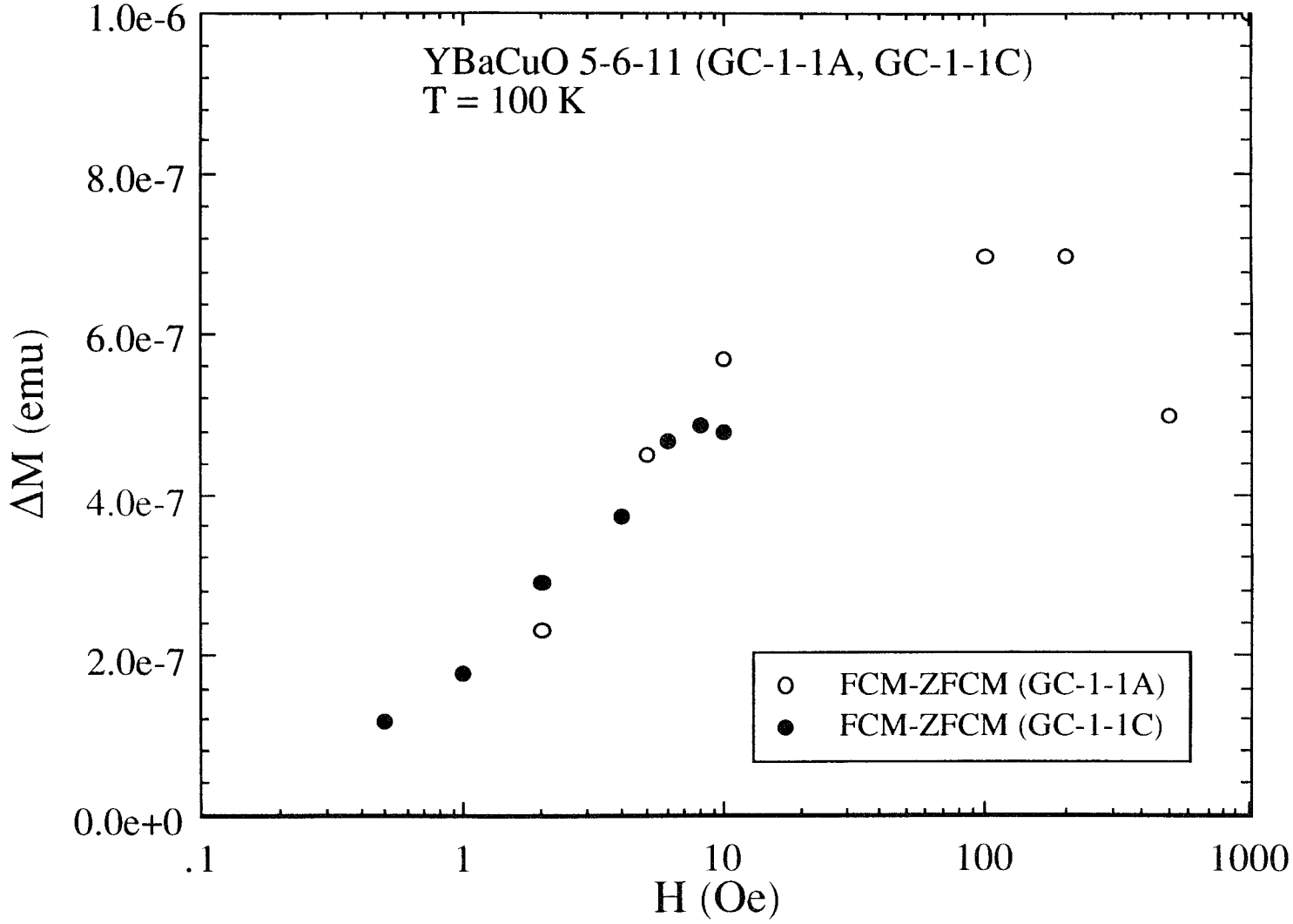

Fig. 5-12. The magnetization difference ΔM (=FCM - ZFCM) as a function of magnetic field for two nominal 5:6:11 YBaCuO samples.